2011

The Synthesis, Reduction, and Chlorination of 5-alkoxy-2,3-diphenylterephthalates

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THE SYNTHESIS, REDUCTION, AND CHLORINATION OF 5-ALKOXY-2,3-DIPHENYLTEREPHTHALATES

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

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B.S., Wright State University, 2009

2011
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WRIGHT STATE UNIVERSITY

SCHOOL OF GRADUATE STUDIES

June 09, 2011

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Rachel M. Sayers ENTITLED The Synthesis, Reduction, and Chlorination of 5-Alkoxy-2,3-diphenylterephthalates. BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science .

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ABSTRACT

Sayers, Rachel M. M.S., Department of Chemistry, Wright State University, 2011. The Synthesis, Reduction, and Chlorination of 5-alkoxy-2,3-diphenylterephthalates.

A series of alkoxy, phenylated terephthalates has been synthesized as monomer precursors to the corresponding poly(phenylene vinylene)s (PPV). The hydroxy, phenylated terephthalate was synthesized via: 1) a Diels-Alder cycloaddition between an ethynyl boronic ester and a cyclopentadienone (CPD) with subsequent hydrolysis/oxidation of the boronate ester or 2) a Diels-Alder cycloaddition between vinylene carbonate and CPD followed by thermolysis of the bridged adduct. The hydroxy, phenylated terephthalate was alkylated via a phase-transfer reaction with iodomethane, propargyl bromide, benzyl chloride, allyl bromide, and bromobutane to produce the alkoxy, phenylated terephthalates in yields from 38.6- 91.1%. The alkoxyterephthlates were reduced with lithium aluminum hydride to either the corresponding 5-alkoxy- (methoxy, benzyloxy) or 5-hydroxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene (allyloxy, propargyloxy) in yields from 40.9-94.0%. The methoxy and benzyloxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzenes were reacted with thionyl chloride to yield the corresponding 1,4-di(chloromethyl)-3,4-diphenylbenzenes. The polymerization of 5-methoxy-1,4-di(chloromethyl)-3,4-diphenylbenzene with *t*-BuOK yielded the insoluble polymer 5-methoxy-2,3-diphenyl-1,4-poly(phenylene vinylene).

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DEDICATION

I would like to dedicate this work to my family; my parents, Susan and Kirk, my sisters, Stephanie and Annie, my friends, Jenny and Kim, and to my fiancé, Matt. Their friendship, love, and support has given me the strength and drive to achieve my goals. I cannot thank them enough for all they have given me.

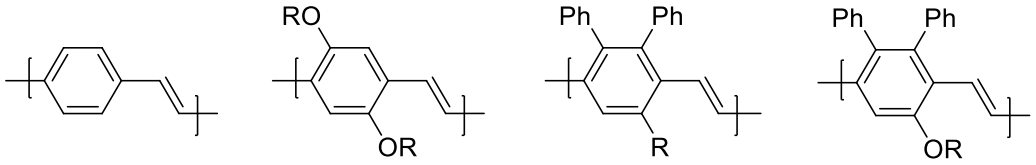
ACKNOWLEDGMENTS

I would like to give a special thanks to my advisor, Dr. William Feld for giving me the opportunity to work in his group. His guidance and teaching inspired me to be a better student and researcher. I would not be the chemist I am today without all that he taught me and for that I am truly grateful.

I would also like to acknowledge the faculty, staff, and graduate students of the Wright State Chemistry Department for all I have learned from them and experienced with them as a student over the past two years.

INTRODUCTION

The conjugated polymer, poly(p-phenylene vinylene) (PPV) **1** and its derivatives **2** and **3** have been of great interest as semiconducting materials due to their ability to transmit charge and emit light when excited.[1]



1 **2** **3** **4**

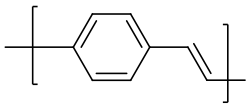
The chemical and thermal stability of the polymer, in addition to the ease of property tuning by the addition of side groups to the main chain, make it highly desired for use in light emitting diode devices such as televisions, computers, and cellular phones.

Insolubility of the unsubstituted polymer **1** has given rise to numerous attempts to synthesize the polymer either by a soluble precursor route, or with the introduction of solubilizing substituents such as phenyl and alkoxy groups. The success in using phenyl and alkyl-substitution to tune the emission properties of **1**[2] and the donor group potential of the alkoxy group in **2**,[3] suggest that a combination of phenyl and alkoxy substitution as in **4**, should lead to enhanced PPV performance.

The purpose of this research was 1) to develop a method for the synthesis of monomers bearing both alkoxy and phenyl side groups on the main chain, 2) to polymerize the monomers to obtain PPV **4**, and 3) to characterize intermediates by melting point, ^{1}H and ^{13}C NMR, IR, and elemental analysis.

HISTORICAL

The electroluminescent properties of conjugated polymers present advantages for use in organic light emitting diodes (OLED) due to their stability, flexibility, and ease of processibility onto large area electrodes via spin coating.[4] Over the years, a great interest in poly(phenylene vinylene)s (PPV) as an organic semiconductor in such devices has developed.

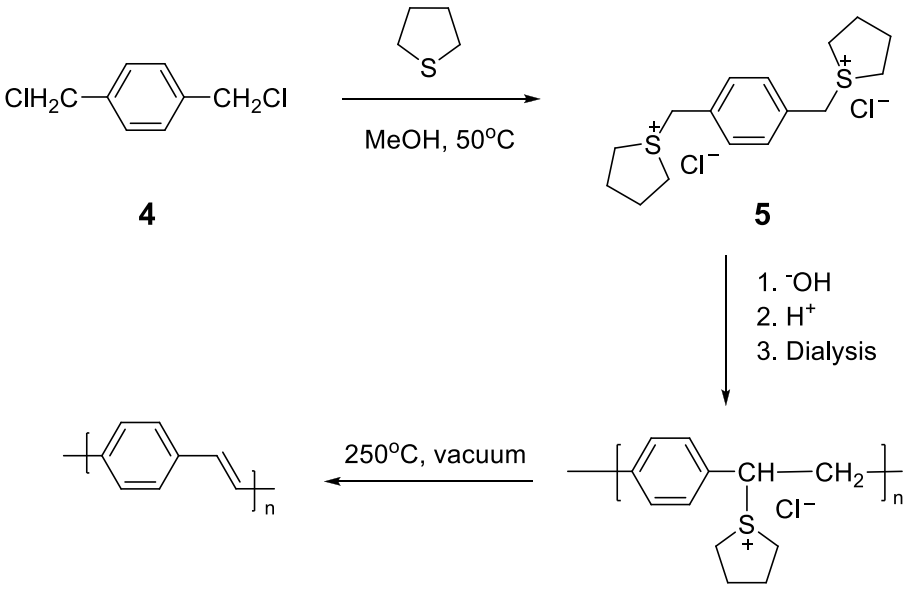


1

In 1990, Burroughes first reported the electroluminescent properties of conjugated polymers, utilizing poly(phenylene vinylene)[1] **1** as the active element in light-emitting diodes. Previous work with inorganic semiconductors, such as GaAs had either lead to efficient light generation that could not be easily or economically used in large area displays or had low efficiency and poor reliability such as systems based on polycrystalline ZnS.[1] Organic molecular semiconductors were of interest because of their high photoluminescence quantum yields. Problems with the long-term stability of the organic films redirected interest toward modifying macromolecular materials. Conjugated polymers were chosen because of their potential ability to provide good charge transport and high luminescence quantum efficiency.

Burroughes synthesized the conjugated polymer **1** using the Sulfonium Precursor Route (SPR) first reported by Wessling in 1967.[5] The soluble precursor polymer **6** was

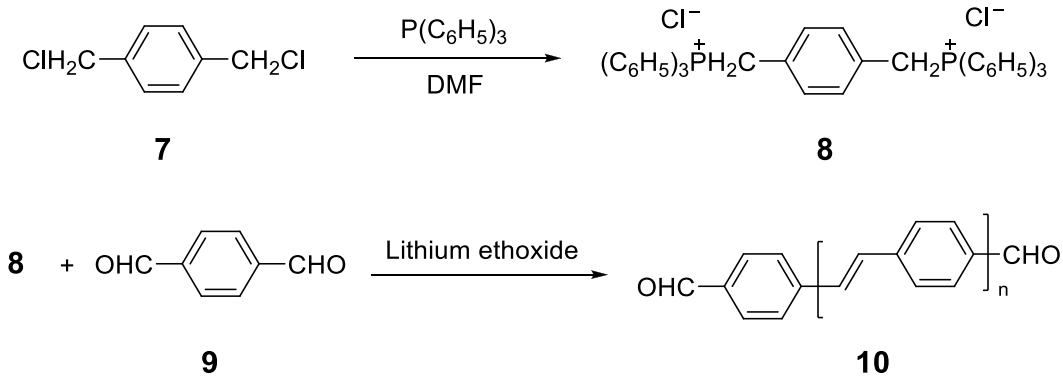
prepared by polymerization of the sulfonium salt intermediate of α, α'-dichloro-*p*-xylene **5** in the presence of base, followed by dialysis of the mixture against distilled water. Thermal conversion of films of the precursor polymer **6** resulted in homogeneous, dense, and uniform films with light emission in the green-yellow region of the spectrum.[1]



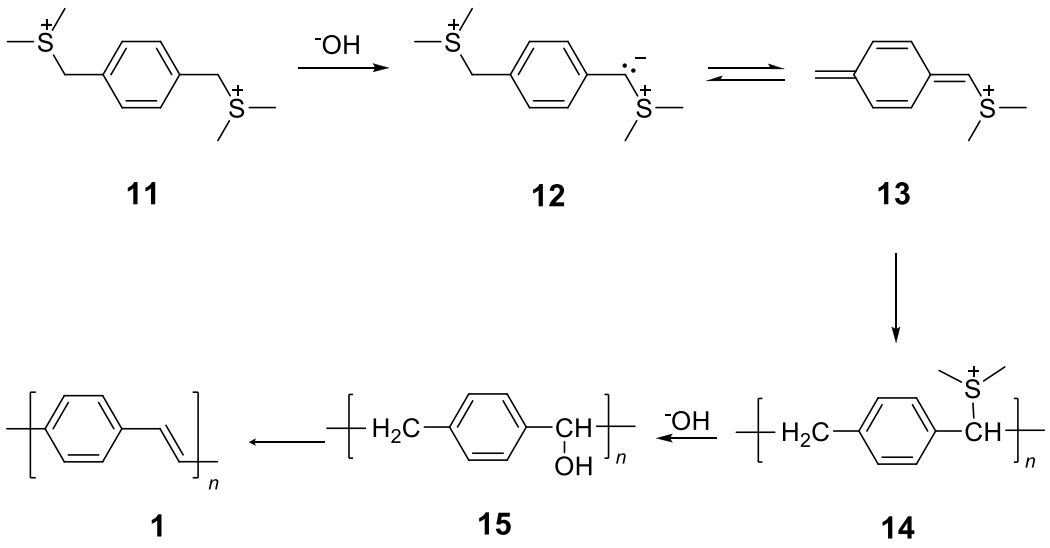
Problems that arise in the unsubstituted PPV **1** are insolubility, intractability, and infusibility. This causes PPVs synthesized directly from a monomer to be insoluble materials, which cannot be further processed into films.[7]

McDonald and Campbell reported one of the earliest methods of PPV synthesis in 1960 utilizing the Wittig reaction.[8] The Wittig reagent, *p*-xylylenebis(triphenyl phosphonium chloride) **8** was synthesized by quaternization of bis(chloromethyl)benzene **7** with triphenylphosphine. The product **8** then participated in a Wittig reaction with terephthalaldehyde **9** in the presence of lithium ethoxide to produce an intense yellow,

insoluble polymer **10**, with a number-average molecular weight of approximately 1200 amu, and carboxaldehyde end groups.[8]

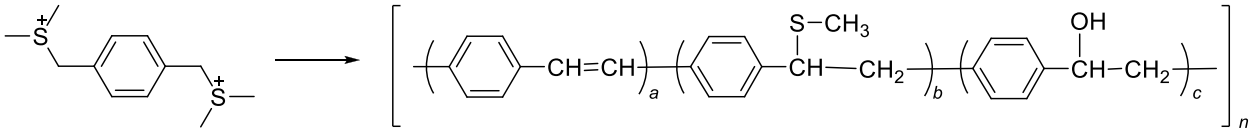


A number of precursor polymerization methods have been employed in order to avoid the insolubility issues associated with the previous PPV syntheses. This allows for thermal or chemical conversion of a soluble precursor to the fully conjugated polymer. Such polymerizations include the Sulfonium Precursor Route (SPR), as used by Burroughes in 1990,[1] the Xanthate Precursor Route (XPR),[9] and the Dehydrochlorination (DHCL) Route.[10]



Wessling first reported the synthesis of PPVs via the Sulfonium Precursor Route (SPR) in 1967.[5] The precursor monomer, bis(di(methylsulfonium)methyl)benzene **11**

reacted with hydroxide ion to yield poly-*p*-xylylidine **1**, also known as PPV.[6] It was presumed that the hydroxide ion first abstracted a proton from **11** to form the ylide **12** which underwent elimination of a di(methylsulfonium) ion to form the monomer precursor **13**. The precursor **13** formed the sulfonium polymer precursor **14** via addition polymerization then underwent a substitution by hydroxide ion to form polymer **15**. Upon elimination of water a polymer, with physical properties similar to poly-*p*-xylylidine **1** was formed.[6] Upon elemental analysis of the polymer, high levels of sulfur and oxygen were found. It was then proposed that a random terpolymer **16** containing **1**,

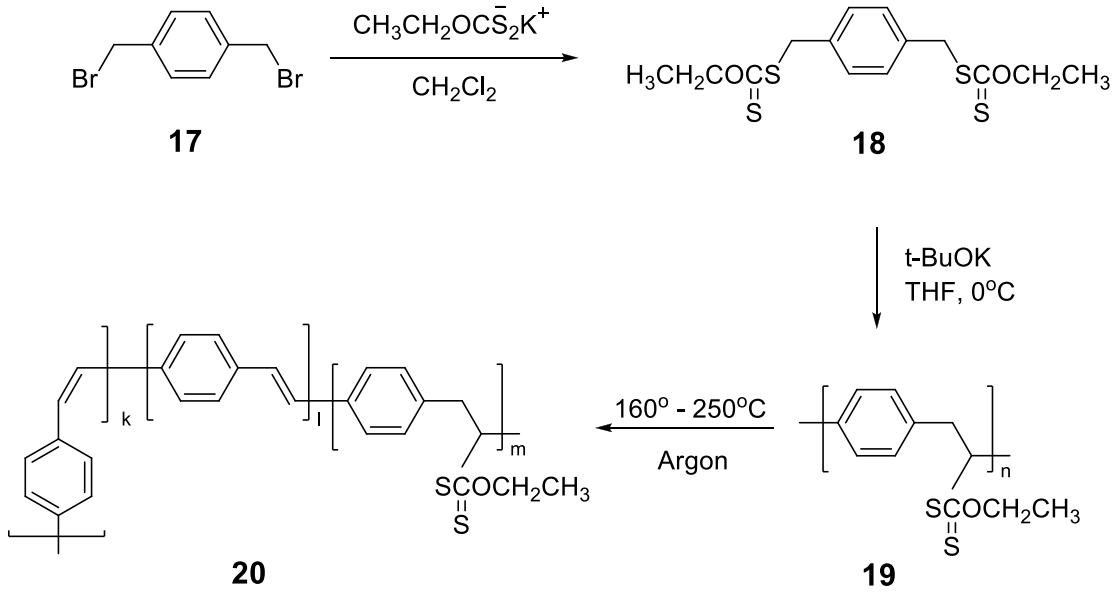


11 **16**

15, and **14**, with one methyl removed by a hydroxide ion, units had formed rather than the fully conjugated polymer **1**.

Problems that arose with the SPR involving the sulfonium precursor polymer hindered both the quality of the films produced and electroluminescence of the polymer. The ionic nature of polymer precursor **11** leads to a polyelectrolyte that may increase in viscosity during polymerization, potentially limiting yields. The precursor **11** is only soluble in polar solvents, which are poor for spin-coating to produce high–quality films.[9] Additionally, as previously observed, using SPR could result in a random terpolymer, such as **16**, with units containing hydroxy groups. These hydroxy groups could be oxidized to carbonyls, limiting the electroluminescence of the polymer after thermal conversion.[9]

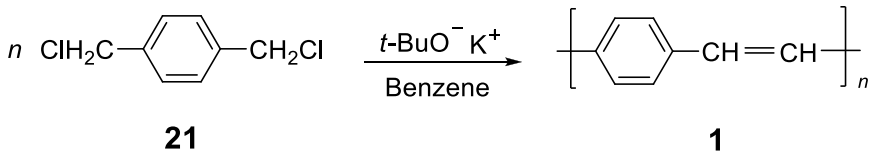
The Xanthate Precursor Route was developed to both manage the problems brought about by polymerization using SPR and to introduce *cis* linkages into the polymer chain.[9] It was proposed that separation of the polymer chains due to the introduction of *cis* linkages would interfere with polymer chain packing, minimizing the quenching sites, which in turn would improve the photoluminescence efficiency of the polymer. The xanthate group on organic soluble precursor **19** could then be eliminated to produce both cis and trans linkages in the polymer chain. In this route, the monomer **18** was synthesized by reacting 1,4-di(bromomethyl)benzene **17** with potassium xanthate.



Monomer **18** was polymerized with potassium *t*-butoxide to make the soluble precursor polymer **19**. Thermal conversion of **19** provided PPV **20** containing cis linkages.[9] Basic devices made with this polymer had significantly higher internal quantum efficiency, 0.22%, than that of Burroughes' device, 0.01%[1], consisting of a Wessling PPV.

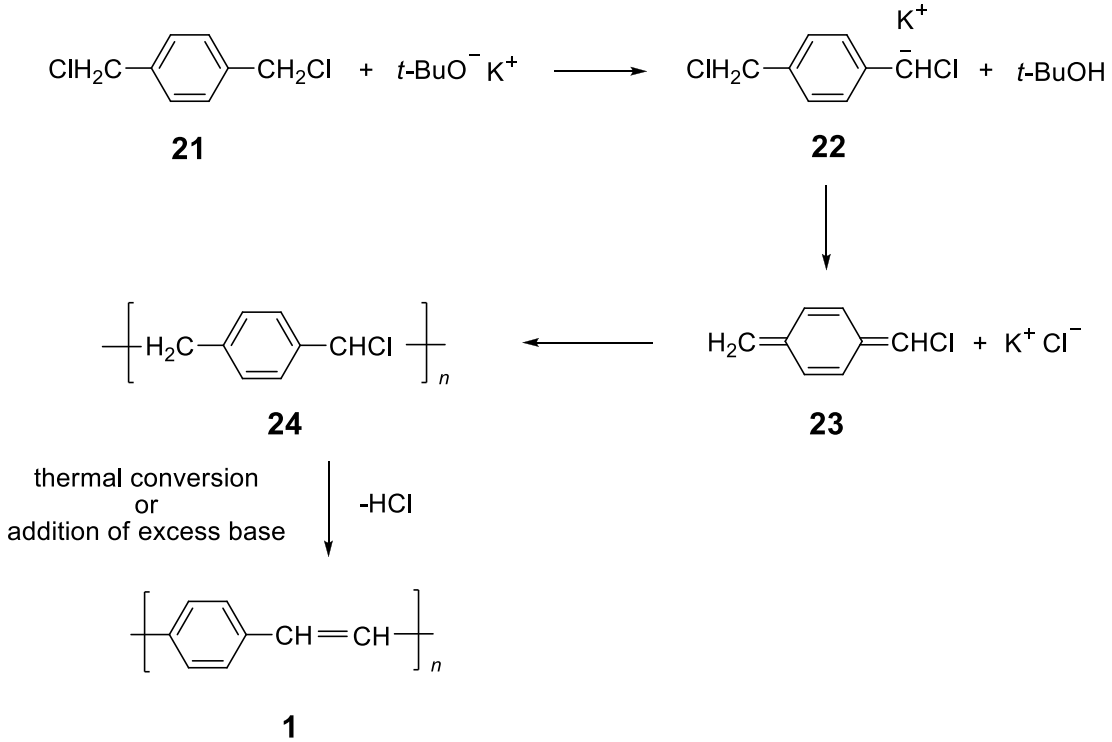
Gilch and Wheelwright were the first to utilize the dehydrochlorination (DHCL) route reacting α,α'-dihalo-*p*-xylene **21** with base to provide PPV **1**.[10] Upon addition of a strong base like potassium *t*-butoxide, a rapid exothermic reaction proceeded in which a

series of reactions occurred to yield a bright yellow solid, with strong ultraviolet fluorescence, and identical properties to polymer **1** synthesized by McDonald and Campbell via the Wittig reaction.



21 **1**

The reaction was proposed to be an addition polymerization, based on the fact that the addition of 30% of the theoretical amount of potassium *t*-butoxide to α,α'-dichloro-*p*-xylene **21** yielded the same polymer as that obtained with an excess of base. In a polycondensation reaction, oligomers would have formed when using a deficient amount of base.[10]



21 **22** **23** **24** **1**

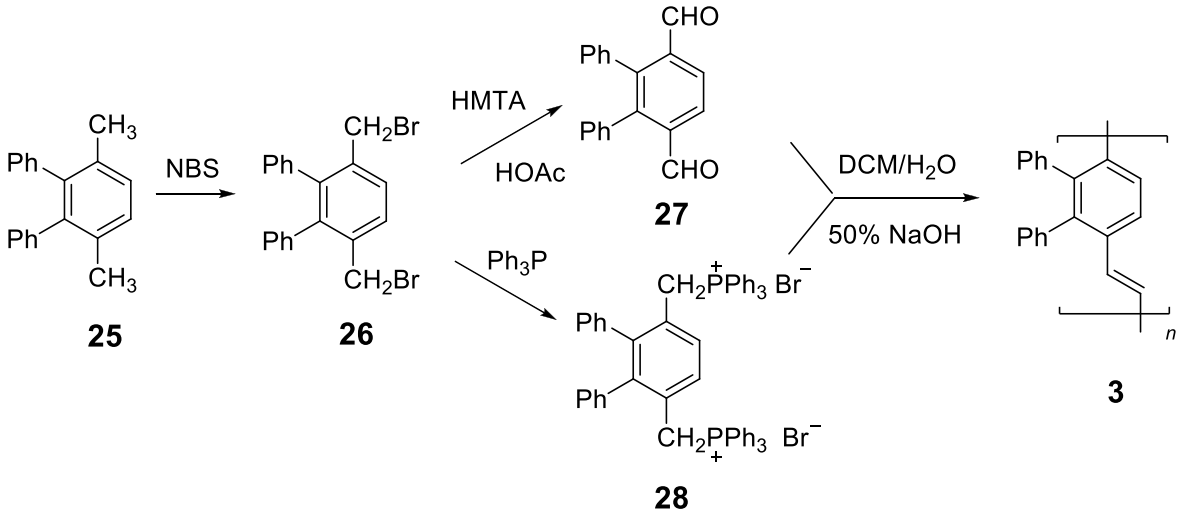
Proposing the type of polymerization that occurred allowed for defining a mechanism. In this method, potassium *t*-butoxide abstracts a proton from α,α'-dichloro-

p-xylene **21** to form the carbanion **22**, which eliminates a chloride ion to form the chloro-*p*-xylylene **23**. Monomer **23** can undergo anionic polymerization with carbanion **22** to form the soluble chlorine precursor **24**. Finally, the precursor is converted to conjugated polymer **1** using an excess of base or heating to eliminate HCl.[10]

Phenylated Poly(p-phenylene vinylene)

Phenylation has been previously reported to increase solubility in a variety of organic compounds including polyphenylenes,[11] imides,[12] quinoxalines,[13] and quinolines.[14] In 1983, the Feld group incorporated pendent phenyl groups into poly(xylylidenes) to increase the solubility of the polymer.[15] A phase transfer catalyzed Wittig reaction was used in an attempt to increase the molecular weight of the corresponding phenylated PPV.

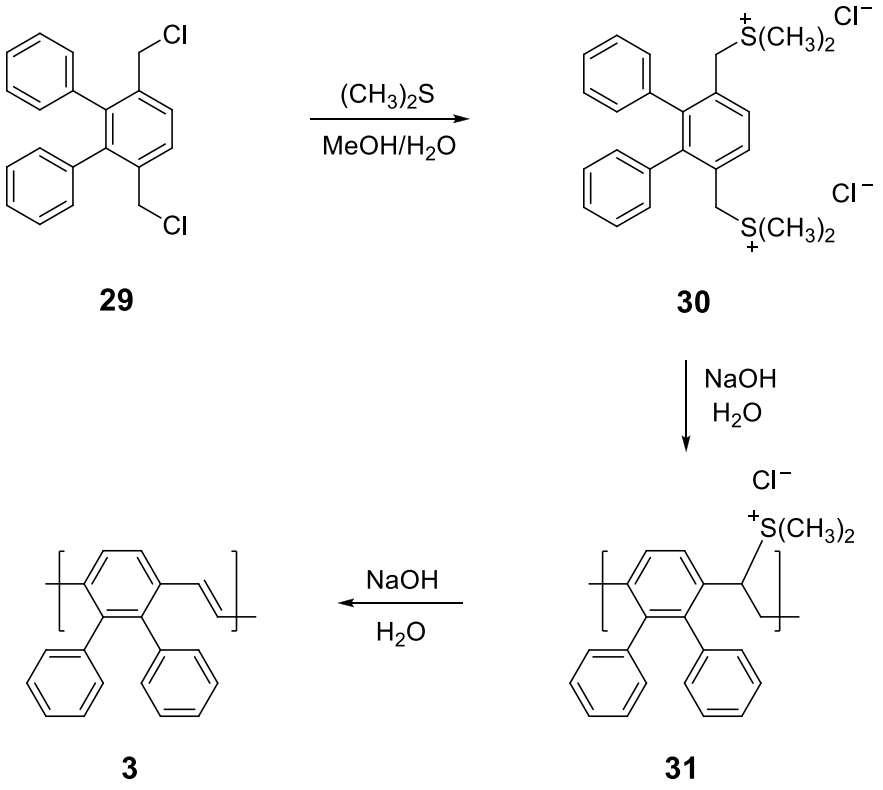
The bromination of 1,4-dimethyl-2,3-diphenylbenzene **25** with NBS yields 1,4-di(bromomethyl)-2,3-diphenylbenzene **26**. To synthesize the two components of the Wittig reaction, the dibromo compound **26** underwent two separate reactions.



25 **26** **27** **28** **3**

First, **26** was converted to 2,3-diphenylterephthaldehyde **27** with hexamethylenetetramine in acetic acid via the Sommelet reaction. In a second reaction,

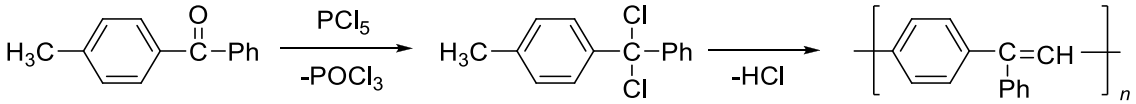
26 reacted with triphenylphospine to form the phenylated bisphosphonium salt **28**. The two monomers **27** and **28** were combined in dichloromethane and mixed with 50% aqueous sodium hydroxide to yield the diphenylated PPV with a molecular weight of 1470 amu as determined by vapor pressure osmometry. It was proposed that in order for polymerization to occur, the phosphonium salt **28,** which acted as both a reagent and the phase transfer catalyst in the reaction, must move into the aqueous layer to be converted to the ylide, which moves back to the organic phase and reacts with a carbonyl. As the polymerization proceeds, it apparently becomes more difficult for the terminal phosphonium groups to move into the aqueous layer preventing the conversion to the ylide, thus inhibiting the generation of high-molecular-weight polymers.[15]



Due to the low molecular weight obtained using the Wittig reaction, attention was turned to the synthesis of **3** via SPR.[16] The reaction began with the treatment of 2,5-

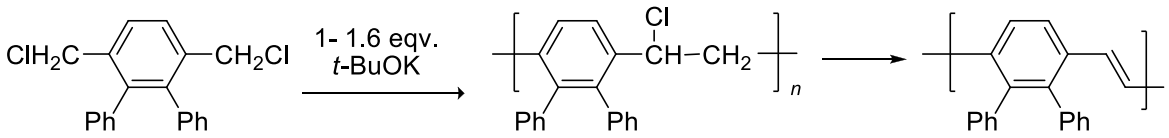
di(chloromethyl)-3,4-diphenylbenzene **29** with dimethyl sulfide in a methanol-water mixture to yield the disulfonium chloride compound **30**. Polymerization was carried out with equimolar amounts of aqueous NaOH to give the sulfonium chloride polymer precursor **31**, which was converted with another equivalent of aqueous NaOH to the conjugated polymer **3** with a minimum molecular weight of 14000 amu.[16]

A related dehydrochlorination (DHCL) route to synthesize a soluble phenylated precursor polymer was introduced by Hörhold in 1986.[17] The polymer was synthesized by reacting 4-methylbenzophenone **32** with phosphorus pentachloride to provide the



32 **33** **34**

dichloro intermediate **33** which was an A-B monomer. Dehydrochlorination was initiated by either heating or addition of pyridine to **33** to produce a bright-yellow solid **34** with strong fluorescence, yields from 39-57%, and molecular weights ranging from 3900-13000 amu.[17]



35 **36** **3**

Hsieh and Feld[18] developed a modified Gilch route known as the Chlorine Precursor Route (CPR) after attempts to polymerize phenylated bis(chloromethyl)benzene **35** with an excess of t-BuOK resulted in gel formation under a variety of conditions as shown in **Table 1**.

Table 1. Polymerization Conditions for Gilch Polymerization.

Run	***Solvent & Volume (mL)***	***Volume (mL)***	***Rate of t-BuOK addition***	***Rate of gel formation***
1	THF (20)	18.0	All at once	Very quickly
2	THF (20)	18.0	Dropwise	Quickly
3	Benzene (40)	18.0	Dropwise	Slower than run #2
4	Benzene (80)	18.0	All at once	30 min later

*All reactions run with 6 eq. of 1.0 M *t*-BuOK in THF

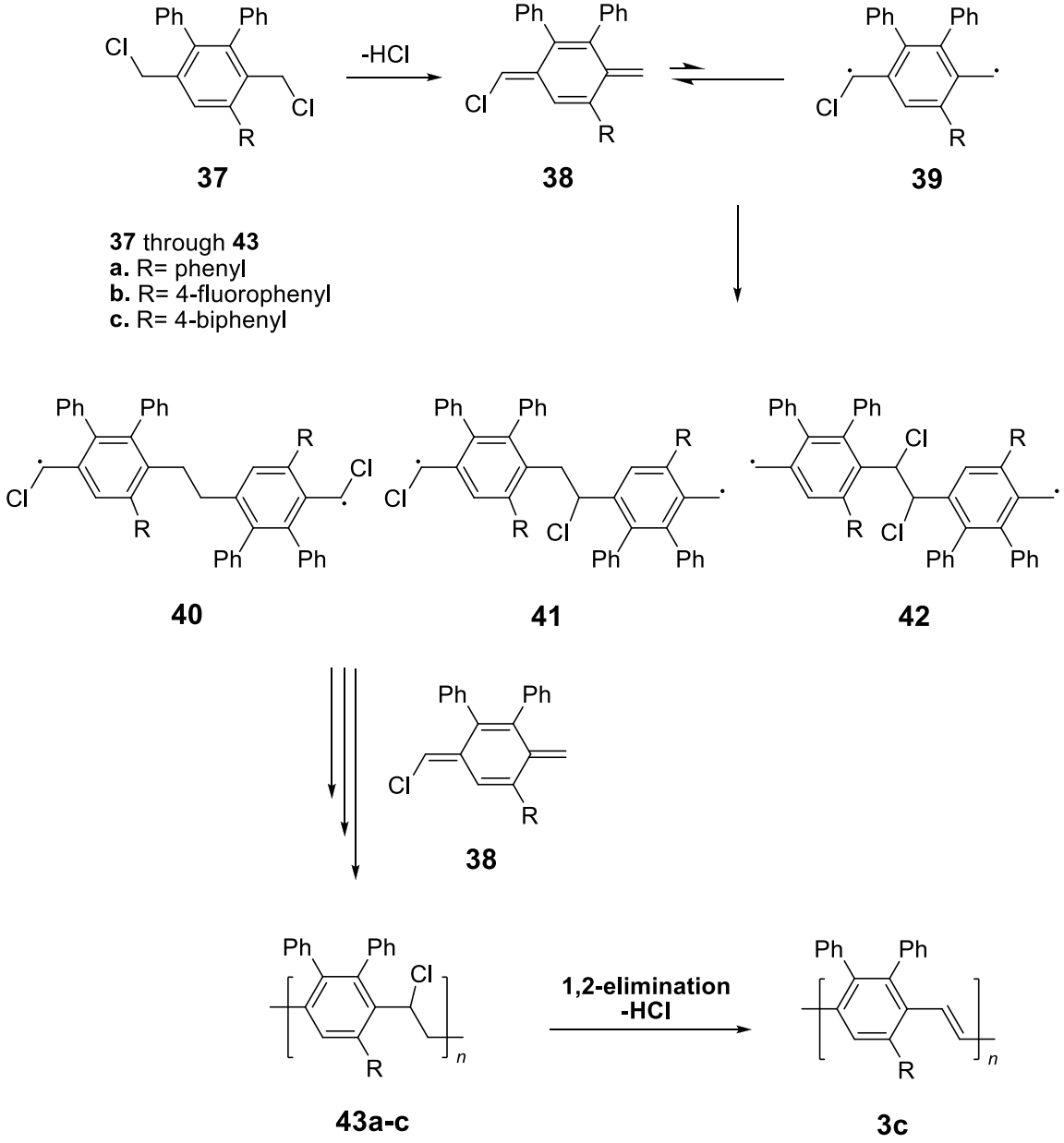
The amount of base used during polymerization was reduced from 6 to 1- 1.6 equivalents to prevent gel formation. The highest molecular weight of polymer **3** was produced when the reaction was carried out in THF with 1.0 eq. of base.[18]

Table 2. Polymerization Conditions and GPC Data for Modified Gilch Polymerization.

Run	***Solvent & Volume (mL)***	***Volume (mL)***	***eq. 1.0 M t-BuOK in THF***	***Mn***	***Mw***	***Mw/ Mn***
5	Benzene (40)	3.5	1.2	19,832	516,135	26.0
6	Benzene (40)	5.0	1.6	111,288	631,285	5.67
7	THF (40)	5.0	1.6	Gel formed quickly		
8	THF (40)	3.0	1.0	211,603	1,118,400	5.29

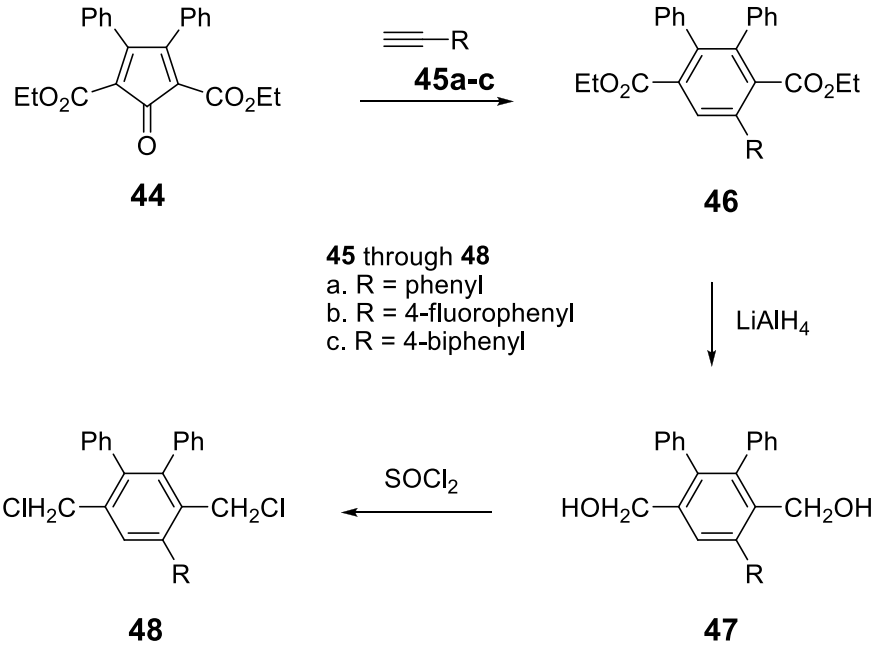
In the synthesis of highly phenylated poly(p-phenylenevinylene)s a radical mechanism was proposed.[19] In this mechanism, the monomer **37** first undergoes 1,6-dehydrochlorination to p-xylylene **38**, which exists in equilibrium with the more reactive diradical **39**. The diradical and/ or *p*-xylylene then form three possible dimer-diradicals, with the tail-tail isomer, **40**, being the most favorable with the least strain energy and the head-head isomer, **42**, being the least favorable with the most strain energy. The dimer-diradicals initiate radical polymerization with **38**, which propagates via the sterically favored head-tail coupling to form the chlorine precursor polymer, **43a-c**. The polymerization of **37a** and **37b** yielded insoluble chlorine polymer precursors, while **37c** yielded a soluble precursor. The spin-coated 4-biphenyl precursor **43c,** upon heating,

underwent a 1,2-elimination of HCl to produce highly phenylated PPV **3c** with number- and weight-average molecular weights of 295,709 amu and 998,557 amu, respectively.



The highly phenylated monomers used by Hsieh and Feld were synthesized by a series of reactions, beginning with a Diels-Alder reaction between 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **44** and a phenylated acetylene **45a-c**.

The substituted dicarboxylates **46a-c** were then reduced with $LiAlH_4$ to the diols **47a-c** and chlorinated with $SOCl_2$ to produce monomers **48a-c**.[19]



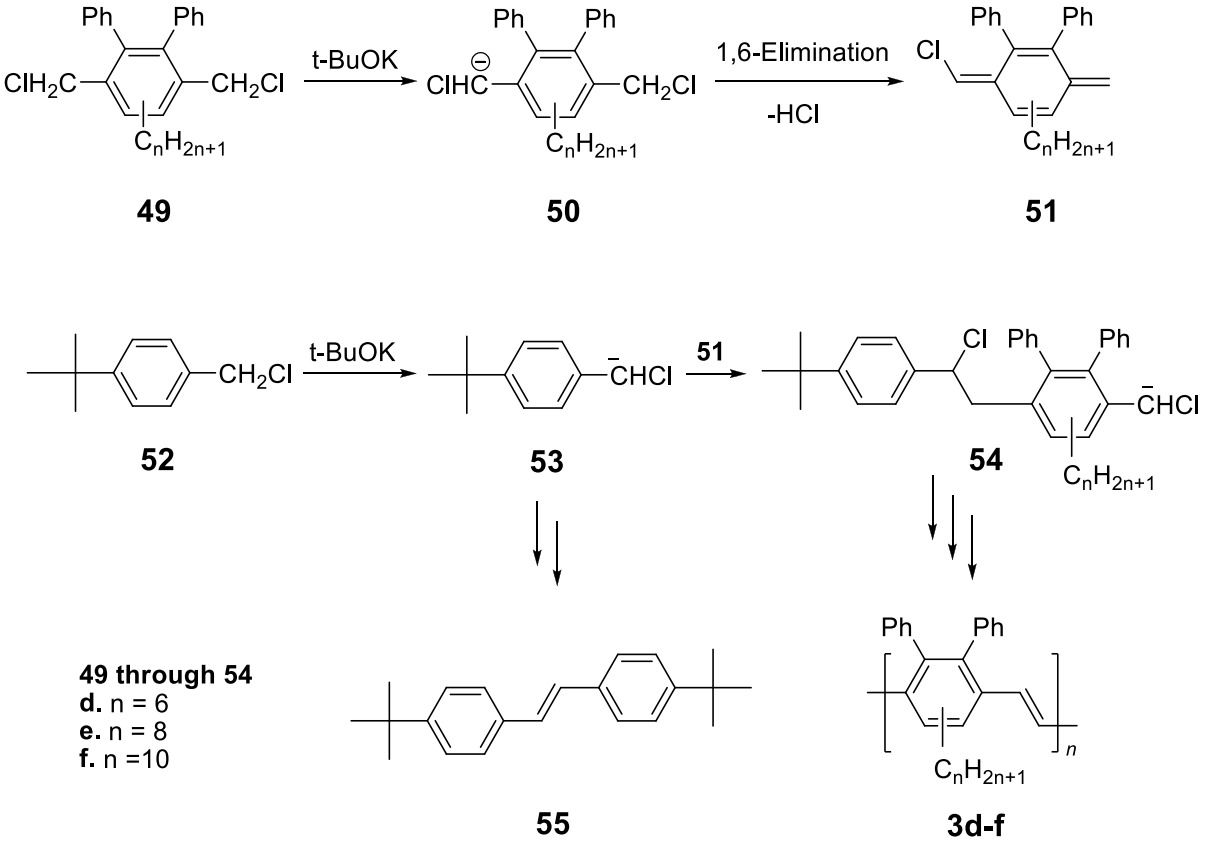
Diphenylated monomers with long alkyl side chains were also synthesized via a Diels-Alder reaction.[2] Polymerization of these alkylated monomers via the Gilch route resulted in gel formation. The non-polymerizable additive, 4-*tert*-butylbenzyl chloride **52**, was added to the reaction to both improve solubility and by varying molar ratios of additive to monomer, control the molecular weight of the polymer.[20]

Table 3. Molar Ratios, Molecular Weights, and Yields of **3d**.

	Monomer	***Molar Ratio 52:49***	***Molecular Weight (x 10^3 amu)***	***Yield***
1	**49d**	-	Gel	-
2	**49d**	0.056	>2000	71
3	**49d**	0.51	1060	66
4	**49d**	0.67	988	50
5	**49d**	1.00	350	45

It was found that as the molar ratio of **52**:**49** increases, the molecular weights of **3d** decrease. This appears to indicate that the reaction proceeds via an anionic

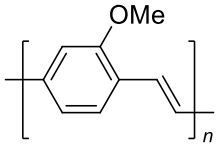
mechanism. One possible anionic mechanism given by Hseih and Feld[2] involves abstraction of the chloromethyl proton of **49** to give the anionic intermediate **50**. The anion undergoes a 1,6-dehydrochlorination to yield the substituted *p*-xylylene **51**. Deprotination of *t*-butylbenzyl chloride **52** produces the anion **53**, which nucleophilically attacks the xylylene **51**, initiating anionic polymerization to yield **3d-f** with *t*-butyl end groups. Additionally, the *tert*-butylbenzyl chloride anions **58** can react with each other to form the side product, 4,4'-di-*tert*-butylstilbene **55**.[2]



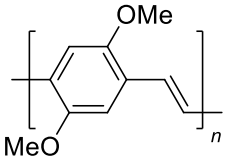
Alkoxy Poly(p-phenylene vinylene)

Poly(phenylene vinylene)s bearing alkoxy side groups have been known to affect both the color emission and solubility of the polymer.[3] Unsubstituted PPV shows a yellow-green photoluminescence (PL)[1] with maxima at 551 nm and 520 nm, while the

monomethoxy PPV **2a** shows yellow emission[21] with a maximum at 550 nm and the 2,5-dimethoxy PPV **2b** emits in the orange-red region[22] with maxima at 603 nm and 650 nm.

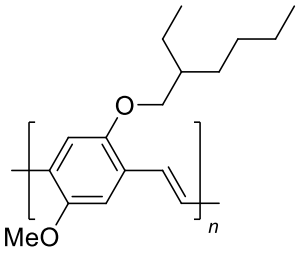


2a



2b

Additionally, polymers with at least one long solubilizing alkoxy chain, such as poly[2-methoxy-5-(2-ethylhexyl)-1,4-phenylene vinylene] **2c**, are soluble in organic solvents

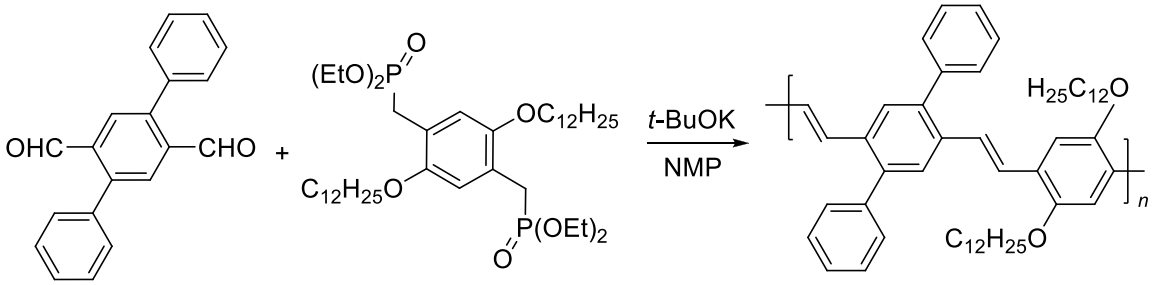


2c

like chloroform, toluene, or tetrahydrofuran.[23] This allows for the fabrication of OLED devices without thermally treating the polymer. The presence of alkoxy groups on the phenylene rings of PPV, as seen on MEH-PPV **2c**, lowers the interchain interactions, which in turn improves the solubility of the polymer in organic solvents.

In 2003, Wu and coworkers incorporated both a phenylated unit and an alkoxy substituted unit into PPV in order to improve emitting efficiency and thermal stability of the polymer.[24] This was achieved via a Horner-Wadsworth-Emmons polycondesation reaction between 2,5-diphenylterephthaldehyde **56** and 2,5-didodecyloxy-*p*-xylylene-bis(diethylphosphonate) **57**. The resulting polymer TP-PPV **58** was found to be fully soluble in common organic solvents, with a weight-average molecular weight of 16,100

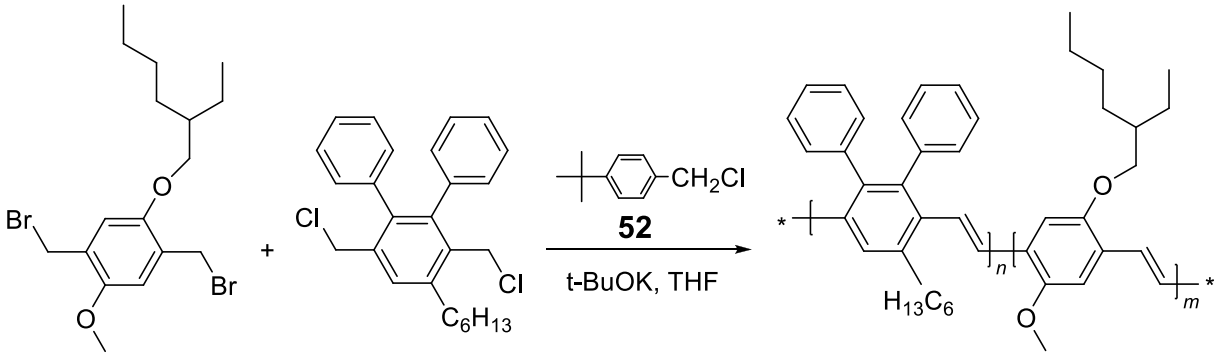
amu, a polydispersity index of 1.41, and a decomposition temperature of 392°C. It was also determined that the copolymer had a PL efficiency of 0.36, larger than that of MEH-



56 **57** **58**

PPV with an efficiency of 0.15.[24] This was attributed to the steric effects of the non-coplanar phenyl rings attached to the phenylene group of the main chain preventing the self quenching of exitons, which leads to increased PL efficiency of the polymer.

At the same time, Chang and coworkers were working towards adjusting color tunability of PPVs through varying the feed ratios of phenylated and alkoxy monomer



59 **60** **61a-e**

derivatives during polymerization.[3] Utilizing the modified Gilch route, a solution of potassium *tert*-butoxide was slowly added to a solution of *tert*-butylbenzyl chloride **52**, and varying concentrations of 2-methoxy-5-ethylhexyloxy-1,4-bis(bromomethyl)benzene

59 and 5-hexyl-1,4-bis(chloromethyl)-2,3-diphenylbenzene **60** in THF to make the copolymers **61a-e** listed in **Table 4**.

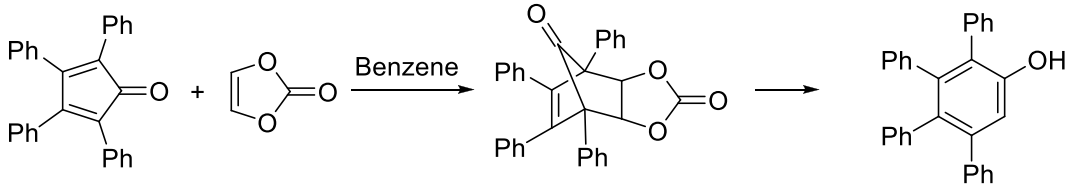
Polymers **61a** and **61e** exhibited light emission wavelengths at 490 and 540 nm, respectively, as previously reported in the literature, while copolymers **61b**, **61c**, and **61d** had wavelength maxima at 530, 545, and 560 nm respectively, providing a series of polymers that emit light in the range of bluish-green to orange.

Table 4: Feed Ratios and Light Emissions of Copolymer **61a-e**.

Polymer	***Feed Ratios (n/m)***	***Light Emission (nm)***
61a	1/0	490
61b	10/1	530
61c	4/1	545
61d	2/1	560
61e	0/1	540

Hydroxy Phenylated Terephthalates

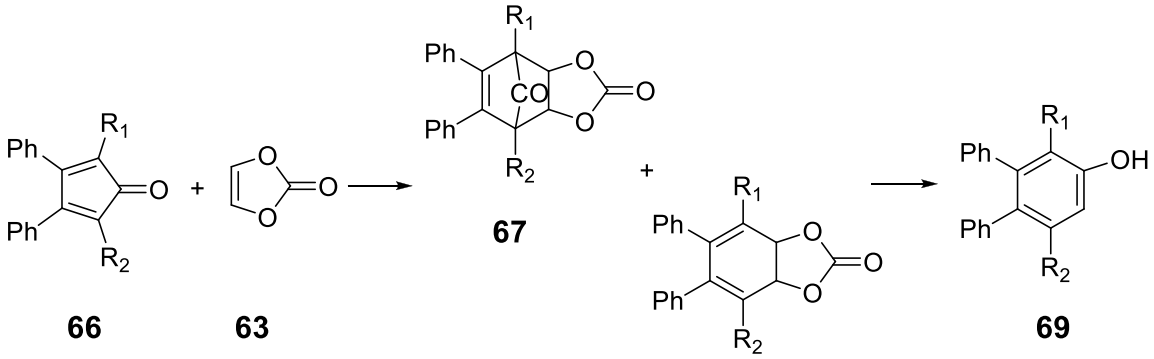
Yate and Hyre first reported the synthesis of a tetraphenyl phenol in 1962.[25] Tetraphenylcyclopentadienone **62** underwent a Diels-Alder reaction with vinylene carbonate **63** in refluxing benzene to produce the bridged adduct **64** at a 60% yield. Upon heating the adduct **64** to its melting point of 208-209°C, gas evolved and 2,3,4,5-tetraphenylphenol **65** was produced in a 95% yield.



62 **63** **64** **65**

In 1975, Harrison synthesized a number of tetrasubstituted cyclopentadienones using this same method, but with different substituents on the cyclopentadienone.[26] A cycloaddition reaction between the substituted cyclopentadienone **66a-d** and vinylene carbonate **63** in refluxing benzene or xylene produced a mixture of the corresponding

bridged adducts **67** and cyclohexadienyl carbonates **68**. Upon thermolysis of products **67** and **68** in bromobenzene, the tetrasubstituted phenol **69** was obtained.[27] In the case of the



66 **63** **67** **68** **69**

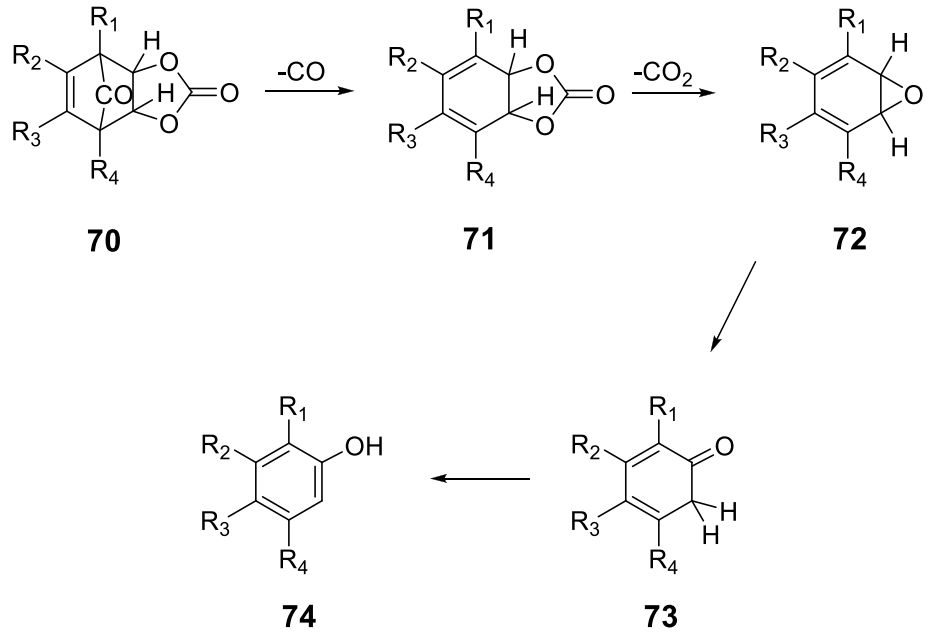
66 through 69
a. $R_1 = R_2 = Ph$
b. $R_1 = Me$; $R_2 = Ph$
c. $R_1 = R_2 = COOMe$
d. $R_1 = R_2 = Me$

diester **66c**; only the cyclohexadienyl carbonate carbonate **68c** was isolated, while a variable mixture of **68c** and **69c** were present in the residual oil. The yield and purity of **69c** was widely variable.

Table 5. Percent Yields Obtained from Conversion from **66a-d** to **69a-d**.

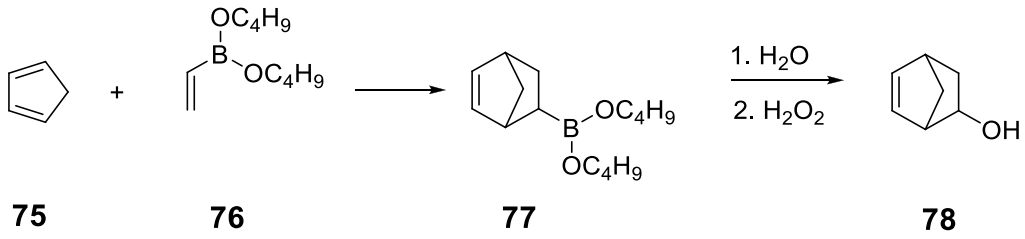
Substrate	***Product***	***Percent Yield (%)***
66a	**69a**	94
66b	**69b**	83
66c	**68c**	34
66d	**69d**	100

After observing the evolution of carbon monoxide and carbon dioxide in the reaction, a mechanism was proposed by Harrison in 1975.[27] This scheme indicates that the benzodioxoledione **70** first loses the carbon monoxide bridge to form the cyclic carbonate **71.** The oxabicycloheptadiene **72,** formed upon the evolution of carbon dioxide, rearranges to the cyclohexadiene **73**, which aromatizes to the tetrasubstituted phenol **74**. This synthetic scheme has not reappeared in the literature since.



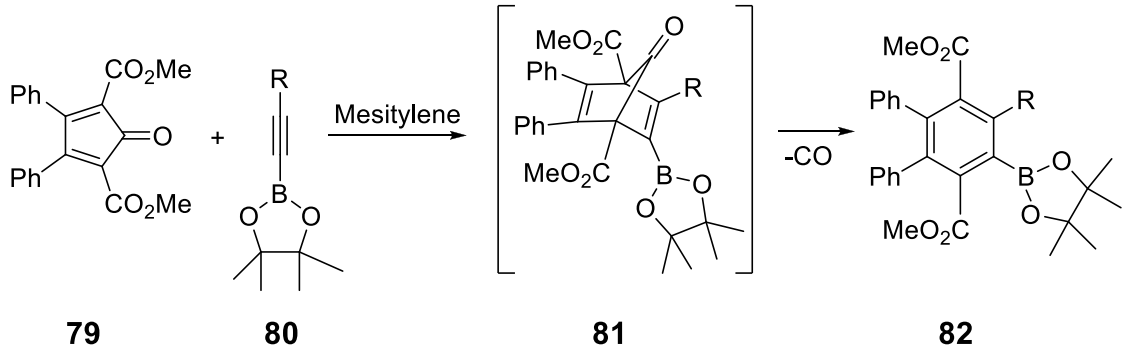
Alkynylboronates

A method to synthesis cyclic alcohols using alkynylboronates was first reported by Matteson and Waldbillig in 1962.[28] For example, a Diels-Alder reaction between cyclopentadiene **75** and dibutyl vinylboronate **76** produced dibutyl 5-norbornene-2-boronate **77.** Hydrolysis of **77** to the boronic acid *in situ* followed by oxidation produced the 5-norbornen-2-ol **78.**



In 2005, Harrity reported a method for synthesizing highly functionalized aromatic boronic esters via a Diels-Alder reaction.[29] The cyclopentadienone **79** and the substituted ethynyl boronic pincacol esters **80a-d** undergo a cycloaddition to form the bridged adducts **81a-d**. Upon evolution of carbon monoxide, the compound aromatizes,

forming the aromatic boronic esters **82a-d** in good yields as illustrated in **Table 6**. There has been no mention of the use of an alkynylboronate in which R=H.

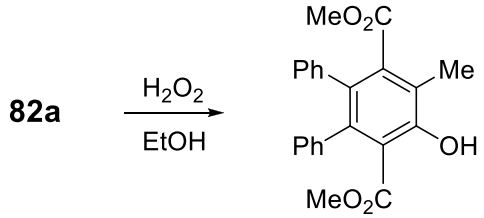


79 **80** **81** **82**

Table 6. R groups and Percent Yields of Cycloaddition Reactions of **80** and **82**.

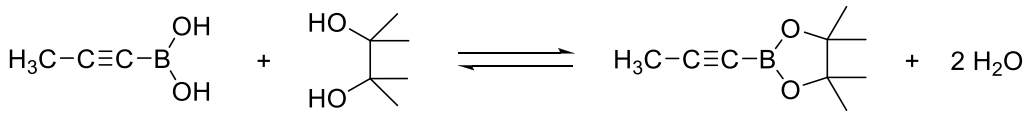
Product	***R***	***Yield (%)***
82a	Me	64
82b	*n*-Bu	59
82c	Ph	58
82d	Me_3Si	58

The methyl substituted aromatic boronic ester **82a** was subsequently oxidized with 30% hydrogen peroxide in ethanol to yield the highly functionalized hydroxy terephthalate **83a** in high yields.



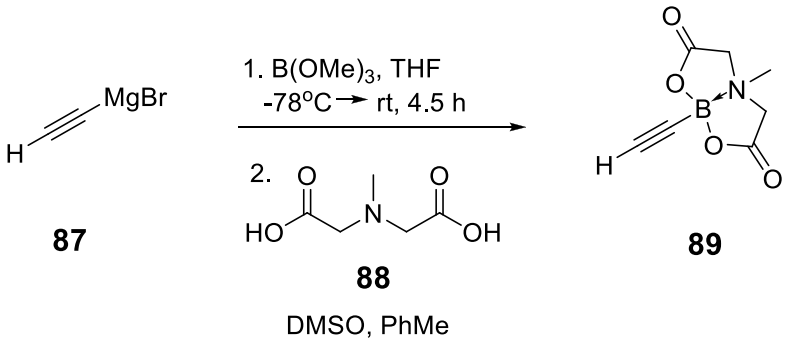
83a

Although ethynyl boronic esters, such as **80a**, are effective dienophiles in the Diels-Alder reaction, they are vulnerable to hydrolysis most likely due to the vacant *p*-orbital on boron.[30] The resulting boronic acid **84** is atmospherically unstable and more difficult to work with.



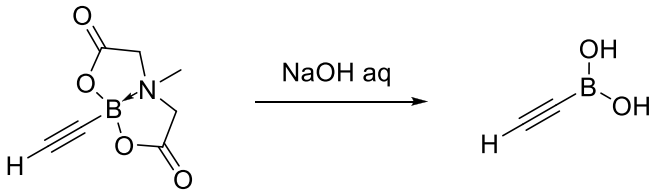
84 **85** **80a** **86**

A more stable alkynyl boronic ester **89** was developed by Burke and reported in 2010.[31] The N-methyliminodiacetic acid (MIDA) **88** protecting group on the boronic acid creates internal coordination between nitrogen and the empty *p*-orbital of the boron, stabilizing the boron against oxidation and making hydrolysis less favorable.[32] These air-stable, free flowing solids are inert towards cross-coupling reactions under anhydrous conditions.



87 **88** **89**

The boronate, ethynylboronic acid MIDA ester **89**, was synthesized by first reacting ethynylmagnesium bromide **87** with trimethyl borate to form the trimethylborate



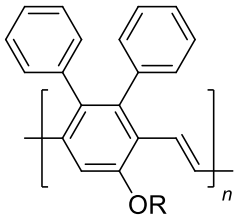
89 **90**

salt. The salt then underwent a condensation reaction with N-methyliminodiacetic acid **88** in DMSO and toluene to form **89** in 51% yield. Even though MIDA boronates such as

89 have good environmental stability, they can be readily hydrolyzed to the boronic acid **90** with mild aqueous base, such as sodium hydroxide.[31]

Alkoxy Phenylated Terephthalates

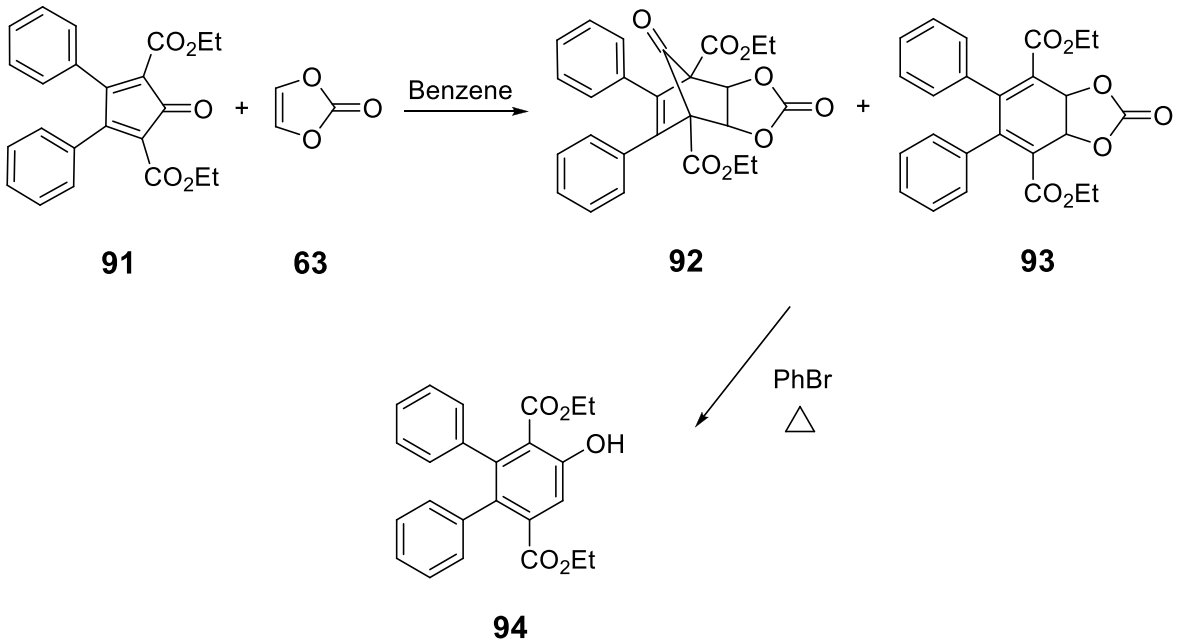
Recently, attention was directed towards the development of a polymer **4** that incorporated both the alkoxy and phenyl substituents on the phenylene group of the



4

backbone.[33] In 2008, Lynette Propyl reported numerous approaches to synthesize monomer precursors bearing two phenyl rings and an alkoxy side chain.

The first approach was to synthesize the hydroxy terephthalate, which could in



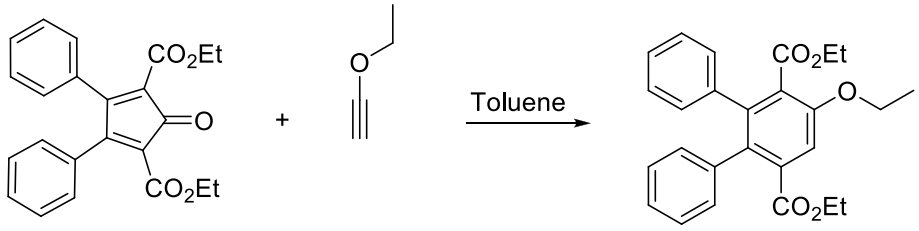
91 **63** **92** **93**

94

principle be alkylated to the desired alkoxy phenyl terephthalate. This approach involved a Diels-Alder reaction between a cyclopentadienone **91** and vinylene carbonate

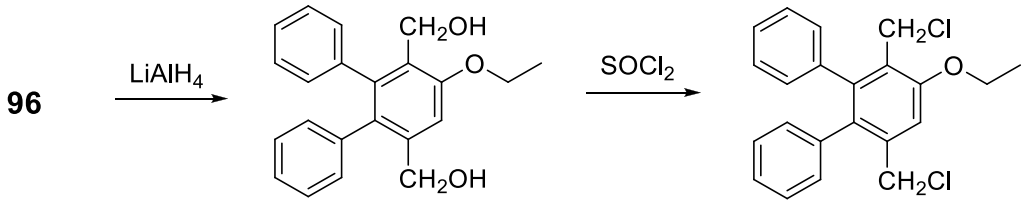
63 in benzene, as initially described by Harrison in 1979.[27] The bridged adduct **92** and substituted cyclohexadiene **93** products were then heated to reflux in bromobenzene to yield the hydroxyterephthalate **94**. Because of the difficulty of reproducing this reaction at the time, alternative methods were pursued.

A second approach involved a more direct synthesis via a Diels-Alder reaction between the cyclopentadienone **91** and ethoxyacetylene **95** to produce the ethoxy terephthalate **96** in a 24% yield.[33] The reaction was expected to proceed via an inverse



91 **95** **96**

electron demand Diels-Alder reaction as a result of the electron withdrawing groups on the diene **91**. While the dienophile, ethyl ethynyl ether **95** is electron donating by resonance; it is also electron withdrawing by inductive effects, which could have hindered cycloaddition between the two reactants. Competitive reactions between **95** and water and limited reaction temperatures due to the low boiling point of **95** could have also contributed to the low yields of **96**.

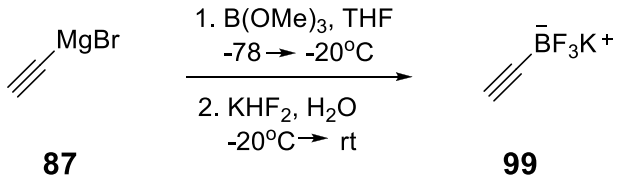


97 **98**

The ethoxy, diphenylterepthalate **96,** was reduced with lithium aluminum hydride

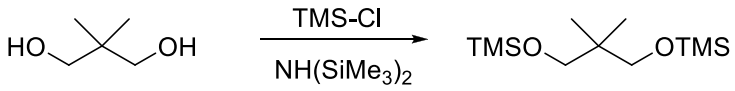
to form the diol **97**, which was chlorinated with thionyl chloride to yield the monomer **98**.[33] Due to low yields in the preparation of **96,** this method was discontinued.

Another approach to synthesize the hydroxy terephthalate was derived from previous reports by Harrity in 2005 involving a [4+2] benzannulation to synthesize highly functionalized aromatic boronic esters. To synthesize the ethynyl boronate **102**,



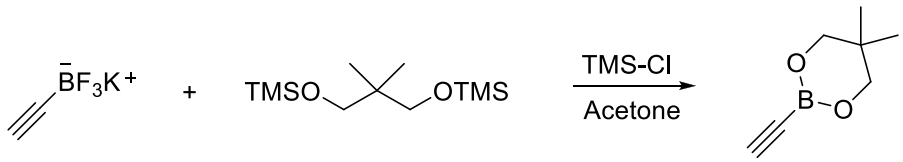
87 **99**

the reagent, potassium ethynyl trifluoroborate **99** first had to be synthesized by reacting ethynyl magnesium bromide **87** with trimethylborate followed by treatment with potassium bifluoride. Difficulties in the isolation of **99** and the high sensitivity of the reagents to moisture attributed to the low yield (49%) of the product.[33]



100 **101**

The second reagent was synthesized by reacting neopentyl glycol **100** with hexamethylsilazane in chlorotrimethylsilane to yield the hydroxy protected neopentyl glycol **101** as an oil (87%).[33]

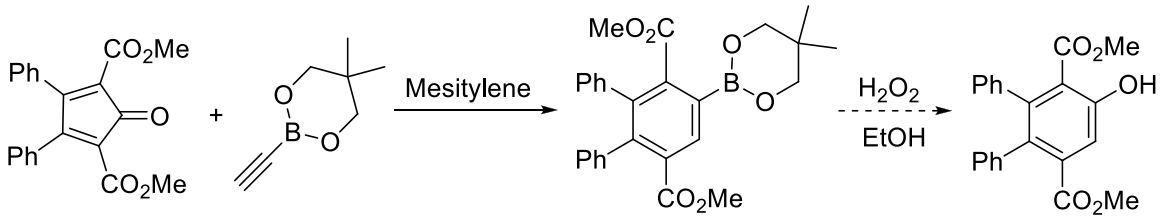


99 **101** **102**

The reagents, potassium ethynyl trifluoroborate **99** and 2,2-dimethyl-1,3-propanediol-bis(trimethylsilyl)ether **101** were reacted in chlorotrimethylsilane overnight

to yield 2-ethynyl-5,5-dimethyl-1,3,2-dioxaborinane **102** as a pale yellow oil with an 83% yield.

The boronate, dimethyl 5-(5',5'-dimethyl-[1',3',2']-dioxaborolan-2-yl)-2,3-diphenylterepthlalate **103**, was then synthesized by a reaction between the cyclopentadienone **79** and the alkynyl boronate **102** in 84% yield and characterized via ^{1}H NMR and ^{13}C NMR.[33] The aromatic boronate **103** could potentially be oxidized with 30% hydrogen peroxide in ethanol to the hydroxy compound **104**.



79 **102** **103** **104**

The purpose of this research was 1) to use/improve upon Harrison's method to synthesize the phenylated hydroxyterephthalate, 2) to explore Harrity's method to synthesize the phenylated hydroxyterephthalate using Burke's MIDA boronate, 3) to alkylate the products of 1 and 2, 4) to reduce and chlorinate the phenylated alkoxyterephthalates, 5) to polymerize the monomer precursors to obtain the corresponding PPV and 6) to characterize intermediates and products by melting point, ^{1}H and ^{13}C NMR, IR, and elemental analysis.

Experimental

Instrumentation and Chemicals. Melting points were obtained with a DigiMelt MPA-160 or Electrothermal MP Apparatus. Nuclear magnetic resonance (NMR) ^{1}H and ^{13}C spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. Solvents for NMR were $CDCl_3$, DMSO-d_6, and Acetone-d_6. Gas Chromatographic-Mass Spectrometric (GC/MS) data was obtained using a Hewlett Packard HP 6890 Series GC System with a 5973 Mass Selective Detector. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing a N_2 atmosphere. Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. X-ray crystallographic data was obtained from the STaRBURSTT Cyberdiffraction Consortium at Youngstown State University using a Bruker-Nonius SMART APEX CCD Diffractometer. Structures were solved using OSCAIL (McArdle, 1995);[34] data collection: SMART (Bruker 2002);[35] cell refinement: SAINT-*Plus* (Bruker, 2003)[36] and CRYSTALS (Betteridge et. al., 2003);[37] program used to solve structures: SHELXS97 (Sheldrick, 2008);[38] program used to refine structure: SHELXS97 (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae et al., 2006);[39] computing publication material: CRYSTALS (Betteridge et. al., 2003). Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. A 35 mL Q-Tube™ (pressure tube reactor) was purchased from Sigma-Aldrich Labware. Chemicals were purchased from Aldrich and used as received.

2,5-Di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone 91

A mixture of benzil **105** (10.5 g, 0.05 mol) and diethyl 1,3-acetonedicarboxylate **106** (12.1 g, 0.06 mol) in absolute ethanol (40 mL) was heated to reflux. A 3.45% (w/v) solution of sodium ethoxide was prepared by dissolving sodium (1.38 g, 0.60 mol) in absolute ethanol (40 mL) and added dropwise to the refluxing mixture. The solution was stirred at reflux for 45 min, with a precipitate forming at approximately 20 min. The solution was cooled and the precipitate was isolated using vacuum filtration and air dried to produce a bright yellow powder **107**. The precipitate was slurried in acetic anhydride (40 mL). Concentrated H_2SO_4 was added dropwise to the mixture until the entire product was dissolved forming a bright-red, gel-like solution. Water was added to the solution 3-4 drops at a time, alternating with 3 drops of H_2SO_4 until the solution temperature began to increase. Water was then added 3-4 drops at a time maintaining a temperature below 80°C. Once the solution had reached room temperature, water (150 mL) was slowly added to the solution to form a light-orange precipitate. The product was stirred for 30 min, filtered, air dried, and recrystallized from high-boiling petroleum ether to yield 15.38 g of bright orange crystals (0.0409 mol, 81.7%): mp. 126.3- 127.9° (lit. 119-121°);[34] IR (NaCl plate, cm^{-1}) 1715, 1729, 2993, 3064, 3384; ^1H NMR ($CDCl_3$, δ) 1.19 (t, 6H, CH_3), 4.20 (q, 4H, CH_2), 7.03-7.40 (m, 10H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 13.91, 61.20, 119.82, 127.72, 128.91, 130.14, 131.00, 162.08, 162.13, 190.96.

Diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate 108

A solution of 2,5-dicarboethoxy-3,4-diphenylcyclopentadienone **91** (0.285 g, 0.757 mmol) and ethynylboronic acid MIDA ester **89** (0.137 g, 0.757 mmol) in toluene (4 mL) was heated in a Q-tube at 170ºC for 24 h. The solution was then cooled and the

volume was reduced in vacuo. The product was washed with absolute methanol and filtered. The product was then recrystallized from acetonitrile/ ethyl acetate (5/95) to yield 0.293 g (80.6%) of a colorless crystal: mp. 222.8- 223.7°; IR (NaCl salt plate) cm^{-1} 1704, 1726, 1781, 2983; ^{1}H-NMR (300 MHz, $CDCl_3$, δ) 0.72 (t, 3H, CH_3), 0.82 (t, 3H, CH_3), 3.13 13 (s, 3H, NCH_3), 3.80 (q, 2H, CH_2), 3.92 (q, 2H, CH_2), 4.32 (d, 2H, NCH_2), 4.42 (d, 2H, NCH_2), 7.00- 7.15 (m, 10H, Ar), 8.00 (s, 1H, Ar); ^{13}C NMR (300 MHz, $Acetone_6$, ppm) 13.59, 13.86, 50.29, 61.37, 61.86, 64.78, 127.43, 127.62, 127.95, 128.03, 130.65, 131.29, 134.19, 134.58, 139.27, 140.02, 142.17, 142.21, 169.23, 169.49, 172.17. Anal. Calcd. for $C_{29}H_{28}BNO_8$: C, 65.8%; H, 5.33%; B, 2.04%; N, 2.65%; O, 24.18%. Found: C, 65.73%; H, 5.32%.

Diethyl 5-hydroxy-2,3-diphenylterephthalate 94

A mixture of absolute ethanol (100 mL) and diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate **108** (0.455 g, 0.856 mmol) was heated and stirred to near boiling until all reactants had dissolved, then cooled. Sodium carbonate (0.098 g, 0.925 mmol) and 30% hydrogen peroxide (15 mL) were added to the solution, and then stirred at rt for 3h. Deionized water (15 mL) was added and the product was extracted with dichloromethane (3 x 15 mL). The organic layers were combined, dried with anhydrous magnesium sulfate, filtered, and reduced. The solid product was recrystallized from 15 mL of absolute ethanol, filtered, and the filtrate was reduced to yield 0.237 g of clear crystals. (0.607 mmol, 70.9%): mp. 108.1-108.7° (lit. 102.6-105.2°);[30] IR (NaCl salt plate) cm^{-1} 1673, 1721, 2983, 3030, 3059; ^{1}H-NMR (300 MHz, $CDCl_3$, δ) 0.67 (t, 3H, CH_3), 0.92 (t, 3H, CH_3), 3.93 (q, 2H, CH_2), 3.99 (q, 2H, CH_2), 6.89- 7.11 (m, 10H, Ar), 7.38 (s, 1H, Ar), 10.70 (s, 1H, OH); ^{13}C-NMR (300 MHz,

$CDCl_3$, ppm) 12.84, 13.53, 61.23, 61.35, 115.24, 116.87, 126.24, 126.32, 126.90, 127.03, 129.52, 130.34, 132.58, 138.28, 138.62, 140.36, 144.08, 159.84, 167.84, 170.53. Anal. Calcd. for $C_{24}H_{22}O_5$: C, 73.83%; H, 5.68%; O, 20.49%. Found: C, 73.92%; H, 5.70%.

4,7-Bis(carboethoxy)-5,6-diphenyl-3a,7a-dihydrobenzodioxol-2-one 92

A solution of vinylene carbonate **63** (1.010 g, 11.7 mmol) and 2,5-dicarboethoxy-3,4-diphenylcyclopentadienone **91** (2.975 g, 7.90 mmol) in benzene (8 mL) was stirred and heated in a Q-tube at 70º for 24 h. The solution was cooled and reduced in vacuo to yield a mixture of the desired product **92** and diethyl 2,3-diphenylterephthalate **109**. The desired product was isolated via recrystallization from benzene/ high boiling petroleum ether to afford 3.02 g (6.50 mmol, 82.3%) of clear crystals: mp. 182.5-183.1ºC; IR (NaCl salt plate) cm^{-1} 1736, 1814, 2984; ^{1}H-NMR (300 MHz, $CDCl_3$, δ) 1.03 (t, 6H, CH_3), 4.17 (q, 4H, CH_2), 5.88 (s, 2H, CH), 7.22-7.26 (m, 10H, Ar); ^{13}C-NMR (300 MHz, $CDCl_3$, δ) 13.69, 62.39, 70.63, 75.67, 128.33, 128.76, 129.26, 131.88, 138.06, 153.85, 164.12, 183.16. Anal. Calcd. for $C_{26}H_{24}O_8$: C, 67.23%; H, 5.21%; O, 27.56%. Found: C, 67.44%; H, 5.01%.

Diethyl 2-oxo-5,6-diphenyl-3a,7a-dihydrobenzo[d][1,3]dioxole-4,7-dicarboxylate 93

A solution of 4,7-bis(carboethoxy)-5,6-diphenyl-3a,7a-dihydrobenzodioxol-2-one **92** (0.155 g, 0.33 mmol) in dry bromobenzene (1.5 mL) was heated at 130° for 18h. The solution volume was reduced under vacuum to yield 0.140 g (0.321 mmol, 97.4%) of white crystals: mp. 166.5- 167.9º; IR (NaCl salt plate) cm^{-1} 1651, 1713, 1811, 2983, 3058; ^{1}H-NMR (300 MHz, $CDCl_3$, δ) 0.85 (t, 6H, CH_3), 3.95 (q, 4H, CH_2), 6.05 (s, 2H, CH), 6.83- 7.09 (m, 10H, Ar); ^{13}C-NMR (300 MHz, $CDCl_3$, δ) 13.39, 61.45, 72.68,

124.89, 127.40, 127.69, 128.50, 136.07, 144.95, 153.39, 165.38. Anal. Calcd. for $C_{26}H_{24}O_8$: C, 69.12%; H, 5.10%; O, 25.78%. Found: C, 69.29%; H, 5.22%.

Diethyl 5-hydroxy-2,3-diphenylterephthalate 94

A solution of 4,7-bis(carboethoxy)-5,6-diphenyl-3a,7a-dihydrobenzodioxol-2-one **92** (0.412 g, 0.887 mmol) in dry bromobenzene (5 mL) was heated at 130° for 5 days. The solution was cooled and the volume was reduced under vacuum to produce an off-white solid. The product was recrystallized from 5 mL of absolute ethanol, filtered, and the filtrate was reduced to yield 0.331g (0.848 mmol, 95.6%) of clear crystals: mp. 107.9-108.5°.

General Procedure for the Synthesis of Diethyl 5-Alkoxy-2,3-diphenylterephthalates 111

A solution of diethyl 5-hydroxy-2,3-diphenylterephthalate **94** (0.250 g, 0.640 mmol) in dichloromethane (5 mL) was added to aqueous sodium hydroxide (0.0607 g in 10 mL). A solution of the appropriate alkyl halide (in excess of 3 eq) and tetra-N-butylammonium bromide (0.315 g, 0.976 mol) in dichloromethane (5 mL) was added dropwise to the first solution and the mixture was stirred overnight (16 h). The mixture was extracted with ethyl acetate (40 mL), which was washed with water (3 x 10 mL), dried over Na_2SO_4, filtered, and the filtrate evaporated in vacuo.

Diethyl 5-methoxy-2,3-diphenylterephthalate 111a

The off-white solid was purified by column chromatography (ethyl acetate/ hexane (25/75)) to yield 0.236 g of colorless crystals (0.583 mmol, 91%): mp. 106.2-107.1°; IR (NaCl plate) cm^{-1} 1731, 2843, 2902, 2938, 2981, 3057, 3444; ^1H NMR ($CDCl_3$, δ) 0.86 (t, 3H, CH_3), 0.90 (t, 3H, CH_3), 3.97 (m, 4H, CH_2), 4.01 (s, 3H, CH_3), 6.93- 7.13 (m, 10H, Ar), 7.38 (s, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 13.43,

13.59, 56.22, 61.15, 110.79, 126.41, 126.99, 127.19, 127.26, 130.01, 130.08, 133.78, 134.53, 137.56, 138.82, 141.01, 154.80, 166.81, 168.44. Anal. Calcd. for $C_{25}H_{24}O_5$: C, 74.24%; H, 5.98%; O, 19.78%. Found: C, 74.27%; H, 5.89%

Diethyl 5-propargyloxy-2,3-diphenylterephthalate 111b

The off-white solid was recrystallized from ethyl acetate/ hexane (25/75) to yield 0.203 g of colorless crystals (0.474 mmol, 74.2%): mp. 107.2- 108.1°C; IR (NaCl plate) cm^{-1} 1732, 2910, 2936, 2982, 3025, 3058, 3290; ^1H NMR ($CDCl_3$, δ) 0.87 (t, 3H, CH_3), 0.92 (t, 3H, CH_3), 2.61 (t, 1H, CH), 3.99 (q, 2H, CH_2), 4.01 (q, 2H, CH_2), 4.85 (d, 2H, OCH_2), 6.94- 7.13 (m, 10H, Ar), 7.54 (s, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) ppm 13.44, 13.62, 56.93, 61.17, 61.21, 76.53, 77.75, 112.59, 126.49, 127.05, 127.21, 127.28, 127.91, 130.00, 130.02, 134.36, 134.74, 137.42, 138.67, 141.22, 152.84, 166.43, 168.17. Anal. Calcd. for $C_{27}H_{24}O_5$: C, 75.68%; H, 5.65%; O, 18.67%. Found: C, 75.58%; H, 5.70%.

Diethyl 5-benzyloxy-2,3-diphenylterephthalate 111c

The off-white solid was recrystallized from ethyl acetate in hexane (25/75) to yield of 0.214 g of colorless crystals (0.447 mmol, 69.8%): mp. 111.9- 113.7°C; IR (NaCl plate) cm^{-1} 1731, 2902, 2936, 2981, 3031, 3058; ^1H NMR ($CDCl_3$, δ) 0.86 (t, 3H, CH_3), 0.93 (t, 3H, CH_3), 3.98 (q, 4H, CH_2), 4.03 (q, 4H, CH_2), 5.26 (s, 2H, OCH_2), 6.95-7.49 (m, 15H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 13.45, 13.68, 61.14, 70.78, 112.31, 126.43, 127.02, 127.15, 127.21, 127.29, 127.84, 128.01, 128.56, 130.01, 130.07, 134.16, 134.39, 136.32, 137.53, 138.82, 141.09, 153.95, 166.73, 168.30. Anal. Calcd. for $C_{31}H_{28}O_5$: C, 77.48%; H, 5.87%; O, 16.65%. Found: C, 77.53%; H, 5.92%.

Diethyl 5-allyloxy-2,3-diphenylterephthalate 111d

The oily product was recrystallized from ethyl acetate/ hexane (25/75) to yield of 0.126 g of colorless crystals (0.295 mmol, 45.9%): mp. 87.1-89.1°; IR (NaCl plate) cm^{-1} 1589, 1648, 1732, 2902, 2936, 2982, 3024, 3058; ^{1}H NMR ($CDCl_3$, δ) 0.76 (t, 3H, CH_3), 0.84 (t, 3H, CH_3), 3.94, 3.89 (q, 2H, CH_2), 4.61 (t, 1H, OCH_2), 4.63 (t, 1H, OCH_2), 5.22 (dd, 1H, CH=C**H**$_2$), 5.37 (dd, 1H, CH=C**H**$_2$), 6.00-6.13 (m, 1H, C**H**=CH_2), 6.83- 7.03 (m, 10H, Ar), 7.27 (s, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$) *δ* 13.44, 13.68, 61.11, 69.62, 112.20, 117.76, 126.41, 126.99, 127.19, 127.26, 127.69, 130.01, 130.07, 132.45, 133.96, 134.37, 137.55, 138.83, 141.03, 153.82, 166.69, 168.34. Anal. Calcd. for $C_{27}H_{24}O_5$: C, 75.33%; H, 6.09%; O, 18.58%. Found: C, 75.31%; H, 6.16%.

Diethyl 5-butoxy-2,3-diphenylterepthalate 111e

The oily product was recrystallized from ethyl acetate/ hexane (25/75) to yield of 0.110 g of colorless crystals (0.247 mmol, 38.6%): mp. 95.3- 96.7°C; IR (NaCl plate) cm^{-1} 1732, 2873, 2935, 2960, 3025, 3058; ^{1}H NMR ($CDCl_3$, δ) 0.86 (t, 3H, C**H**$_3$), 0.97 (t, 3H, OCH_2C**H**$_3$), 0.99 (t, 3H, OCH_2C**H**$_3$), 1.51 (sextet, 2H, C**H**$_2$$CH_3$), 1.82 (quintet, 2H, CH_2C**H**$_2$$CH_2$), 3.98 (q, 2H, C**H**$_2$), 4.02 (q, 2H, C**H**$_2$), 4.15 (t, 2H, OC**H**$_2$), 6.93- 7.13 (m, 10H, Ar), 7.35 (s, 1H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 13.44, 13.71, 13.75, 19.12, 60.99, 61.08, 68.77, 111.70, 126.35, 126.94, 127.17, 127.24, 127.53, 130.02, 130.10, 133.53, 134.42, 137.60, 138.93, 140.85, 154.35, 166.78, 168.51. Anal. Calcd. for $C_{28}H_{30}O_5$: C, 75.31%; H, 6.77%; O, 17.92%. Found: C, 75.09%; H, 6.72%.

General Procedure for the Synthesis of Diethyl 5-Alkoxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112

Lithium aluminum hydride (0.164 g, 4.0 mmol) was slowly added to a 3-neck round-bottomed flask containing anhydrous THF (10 mL) cooled to 0°C under nitrogen. Using an addition funnel, the appropriate diethyl 5-alkoxy-2,3-diphenylterephthalate **111** (0.752 mmol) in anhydrous THF (5 mL) was added dropwise to the stirring solution. The solution was warmed to rt and stirred for 1 h, then heated to 70° under reflux for 16 h. To the grey mixture, H_2O (2 mL) was added to remove any unreacted $LiAlH_4$. To the solution, 15% aqueous NaOH (2 mL) was added followed by 10% H_2SO_4 (2 mL). The product was then extracted with dichloromethane, which was evaporated to yield a white solid.

5-Methoxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112a

The solid was recrystallized from aqueous isopropanol to yield 0.226 g of white powder (0.707 mmol, 94%): mp. 195.3-196.7°; ^{1}H NMR (DMSO, δ) 3.89 (s, 3H, CH_3), 4.14 (d, 2H, CH_2), 4.16 (d, 2H, CH_2), 4.28 (t, 1H, OH), 5.11 (t, 1H, OH), 6.89- 7.14 (m, 10H, Ar), 7.33 (s, 1H, Ar); ^{13}C NMR (300 MHz, DMSO, ppm) 55.48, 55.53, 61.21, 108.07, 125.56, 125.95, 125.98, 126.82, 127.29, 130.21, 131.27, 139.03, 139.05, 140.55, 142.32, 157.13. Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.73%; H, 6.29%; O, 14.98%. Found: C, 78.95%; H, 6.50%.

5-Hydroxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112b from Diethyl 5-propargyloxy-2,3-diphenylterephthalate 111b

The solid was recrystallized from ethanol to yield 0.094 g of clear crystals (0.308 mmol, 40.9%): mp. 181.4- 182.0°; ^{1}H NMR (DMSO, δ) 4.08 (d, 2H, C**H**$_2$OH), 4.18 (d, 2H, C**H**$_2$OH), 4.52 (t, 1H, CH_2O**H**), 5.01 (t, 1H, CH_2O**H**), 6.87- 7.13 (m, 11H, Ar), 9.51

(s, 1H, OH); ^{13}C NMR (300 MHz, DMSO, ppm) 56.68, 61.03, 112.48, 123.32, 125.77, 125.87, 126.84, 127.22, 129.77, 129.88, 130.15, 130.33, 139.30, 139.34, 140.24, 141.80, 155.40.

5-Benzyloxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112c

The solid was recrystallized from aqueous isopropanol to yield 0.230 g of clear crystals (0.580 mmol, 77%): mp. 170.2-171.0°; IR (NaCl plate) cm^{-1} 2341, 2359, 3309; ^{1}H NMR (Acetone$_6$, δ) 3.30 (t, 1H, OH, J = 6 Hz), 4.12 (t, 1H, OH, J = 6 Hz), 4.35 (d, 2H, CH_2, J = 6 Hz), 4.43 (d, 2H, CH_2, J = 6 Hz), 5.32 (s, 2H, CH_2), 6.97-7.64 (m, 11H, Ar); ^{13}C NMR (300 MHz, DMSO, ppm) 55.68, 61.15, 69.54, 109.38, 125.80, 126.06, 126.88, 127.27, 127.33, 127.76, 128.40, 130.16, 131.61, 137.45, 138.90, 138.96, 140.49, 142.53, 156.29. Anal. Calcd. for $C_{27}H_{24}O_3$: C, 81.79%; H, 6.10%; O, 12.11%. Found: C, 81.85%; H, 6.15%.

5-Hydroxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112b from Diethyl 5-allyloxy-2,3-diphenylterephthalate 111d

The solid was recrystallized from ethanol to yield 0.109 g of white powder (0.357 mmol, 47.5%): mp. 181.4- 182.0°; ^{1}H NMR (DMSO, δ) 4.09 (d, 2H, C**H**$_2$OH), 4.19 (s, 2H, C**H**$_2$OH), 4.53 (s, 1H, CH_2O**H**), 5.01 (t, 1H, CH_2O**H**), 6.87-7.14 (m, 11H, Ar), 9.52 (s, 1H, O**H**); ^{13}C NMR (300 MHz, DMSO, ppm) 56.71, 61.05, 112.49, 123.32, 125.78, 125.88, 126.85, 127.23, 129.89, 130.16, 130.34, 139.30, 139.35, 140.25, 141.81, 155.42. Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.41%; H, 5.92%; O, 15.67%. Found: C, 78.15%; H, 6.08%.

5-Hydroxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene 112b from Diethyl 5-hydroxy-2,3-diphenylterephthalate 94

Lithium aluminum hydride (0.183 g, 4.82 mmol) was slowly added to a 3-neck round bottom flask containing anhydrous THF (10 mL) cooled to 0° under nitrogen. Using an addition funnel, diethyl 5-hydroxy-2,3-diphenylterephthalate **94** (0.292 g, 0.748 mmol) in anhydrous THF (5 mL) was added dropwise to the stirring solution. The solution was warmed to rt and stirred for 1 h, then heated to 70° under reflux for 16 h. To the grey mixture, H_2O (2 mL) was added to remove any unreacted $LiAlH_4$. To the solution, 15% aqueous NaOH (2 mL) was added followed by 10% H_2SO_4 (2 mL). The product was then extracted with dichloromethane, which was evaporated to yield a 0.111 g of white solid. (0.362 mmol, 48.4%): mp. 181.4- 182.0°; ^{1}H NMR (DMSO, δ) 4.09 (s, 2H, C**H**$_2$OH), 4.19 (s, 2H, C**H**$_2$OH), 4.63 (s, 1H CH_2O**H**), 5.02 (s, 1H, O**H**), 6.87- 7.11 (m, 10H, Ar), 7.14 (s, 1H, Ar); ^{13}C NMR (300 MHz, DMSO, ppm) 56.73, 61.05, 112.50, 123.32, 125.78, 125.88, 126.85, 127.23, 129.77, 129.90, 130.16, 130.34, 139.30, 139.35, 140.25, 141.81, 155.42.

General Procedure for the Synthesis of Diethyl 5-Alkoxy-1,4-di(chloromethyl)-3,4-diphenylbenzene 113

Thionyl chloride (1.044 g, 8.78 mmol) was added slowly to the respective 5-alkoxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene **112** (0.617 mmol) in a 10 mL RBF cooled to 0°. The solution was warmed to rt then stirred for 1 h. The solution was then heated to 50° and stirred for 1 h. The solution was cooled to rt and continued to stir overnight. The dark brown solution was then poured into 20 mL of deionized water and stirred overnight. The brown solid was then extracted with dichloromethane (3 x 35 mL). The organic layer was separated and evaporated in vacuo.

5-Methoxy-1,4-di(chloromethyl)-3,4-diphenylbenzene 113a

The light-red solid was purified by column from ethyl acetate/ hexane (40/60) to yield off-white crystals (0.178 g, 0.498 mmol, 80.7%): mp. 108.4- 109.8°; IR (NaCl plate, cm^{-1}) 1329, 2839, 2937, 2963, 3023, 3056; ^{1}H NMR ($CDCl_3$, δ) 3.94 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 4.34 (s, 2H, CH_2), 6.90-7.08 (m, 10H, Ar), 7.18 (s, 1H, Ar), ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 39.45, 44.89, 56.03, 111.08, 124.86, 126.70, 126.86, 127.41, 127.54, 130.18, 130.54, 134.32, 137.19, 138.08, 143.94, 157.29. Anal. Calcd. for $C_{21}H_{18}Cl_2O$: C, 70.60%; H, 5.08%; Cl, 19.85%; O, 4.48%. Found: C, 70.86%; H, 5.24%.

5-Benzyloxy-1,4-di(chloromethyl)-3,4-diphenylbenzene 113b

The off-white solid was purified by column from ethyl acetate/ hexane to yield 0.097 g of white crystals (0.224 mmol, 36.2%): mp. 110.6- 111.7°; IR (NaCl plate, cm^{-1}) 1591, 1810, 1879, 1952, 2868, 2930, 2976, 3029, 3058; ^{1}H NMR ($CDCl_3$, δ) 4.39 (s, 2H, C**H**$_2$Cl), 4.51 (s, 2H, C**H**$_2$Cl), 5.32 (s, 2H, CH_2), 7.03- 7.63 (m, 15H, Ar); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 39.57, 44.89, 70.49, 112.22, 125.21, 126.73, 126.90, 127.31, 127.45, 127.56, 128.06, 128.68, 130.02, 130.52, 134.52, 136.68, 137.16, 138.06, 144.00, 156.40. Anal. Calcd. for $C_{27}H_{22}Cl_2O$: C, 74.83%; H, 5.12%; Cl, 16.36%; O, 3.69%. Found: C, 74.69%; H, 5.27%.

Poly(5-methoxy-1,4-phenylene vinylene) 114

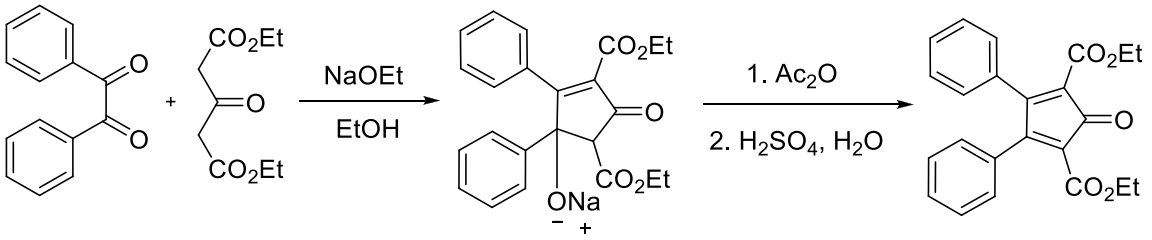
In a 3-neck 25 mL RBF, 1-methoxy-2,5-bis(methylchloro)-3,4-diphenylbenzene (0.478 g, 1.334 mmol) was dissolved in anhydrous THF (5 mL) and cooled to 0°. 4-*t*-butylbenzyl chloride (0.362g, 1.98 mmol, 1.48 eq) was added to the flask with anhydrous THF (5 mL). Under nitrogen, 1.0 M potassium t-butoxide in THF (7.0 mL) was added rapidly to the solution to produce an orangish-brown solution. The solution was warmed

to rt and continued to stir under nitrogen for 10 min and a yellow gel formed. The nitrogen was removed and the gel continued to stir for 24 hr. The gel was then poured into 200 mL of methanol using THF to remove the remaining gel from the flask. The methanol mixture was stirred for 1.5 h then filtered and air-dried to yield 0.321 g (1.07 mmol, 80.1%) of orange solid: mp. 125.94°; IR (NaCl plate, cm^{-1}) 1601, 2834, 2934, 2994, 3022, 3055. TGA of the polymer showed 5% weight loss at 381.47°.

RESULTS AND DISCUSSION

The Diels-Alder reaction was used to synthesize alkoxy-phenylated terephthalates because it has been shown to be useful in introducing a variety of pendent groups into terephthalates. Alkoxy-phenylated terephthalates are expected to undergo further reactions to provide monomer precursors for alkoxy-phenylated poly(phenylene vinylene)s.

The cyclopentadienone, 2,5-di(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **91**, was synthesized by a two-step aldol condensation. In a solution of ethanol and sodium ethoxide, benzil **105** and 1,3-acetonedicarboxylate **106** were reacted to form the sodium salt **107**. The salt was dehydrated in acetic anhydride with sulfuric acid to provide **91**.



105 **106** **107** **91**

The IR spectrum of the compound **91** exhibited two significant absorptions at 1715 cm^{-1} and 1729 cm^{-1} (**Figure 35**), which were attributed to the carbonyl peaks of the ketone and ethyl esters, respectively.

The ^{1}H NMR spectrum of **91** (**Figures 33 and Table 7**) exhibited a triplet absorption at 1.19 δ and a quartet absorption at 4.20 δ corresponding to the six methyl

protons and the four methylene protons of the ethyl groups as illustrated in **Figure 1** and **2**. The multiplet absorption ranging from 7.03 to 7.50 δ corresponds to the ten aromatic protons of the attached phenyl groups.

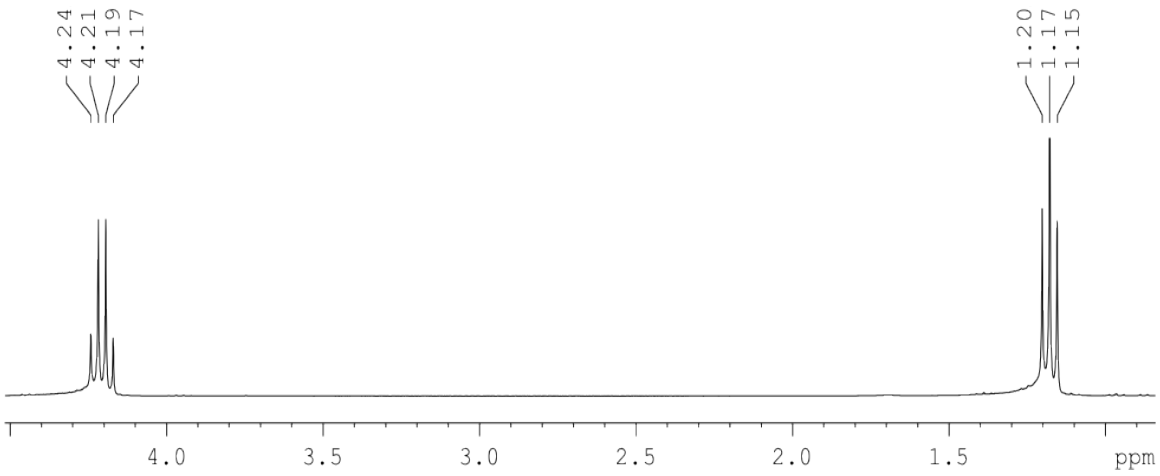


Figure 1. Expanded aliphatic region of the NMR spectrum of **91**.

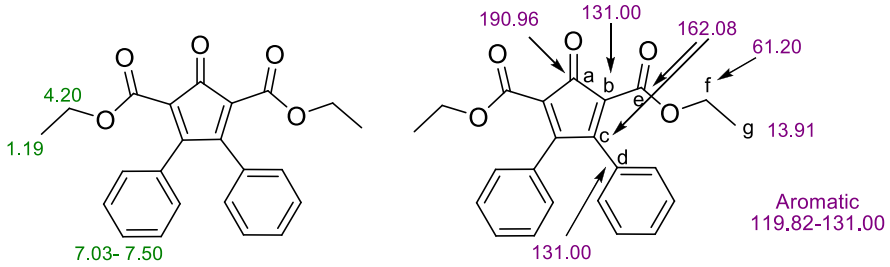
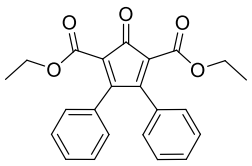


Figure 2. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **91**.

The carbon atoms of **91** were identified using ^{13}C NMR spectroscopy (**Figures 2** and **34**). Absorptions corresponding to the primary and secondary carbons of the ethyl groups were present at 13.91 (g) and 61.20 ppm (f), respectively. Carbonyl absorptions were found at 190.96 ppm (a), attributed to the ketone of the five-membered ring and at 162.08 ppm, attributed to overlapping absorptions of the aromatic carbons (c) and (e) of the cyclopentadienone. The remaining five absorptions in the range of 119.82- 131.00

ppm were attributed to the twelve aromatic carbons with overlapping of two quaternary absorptions, possibly at 131.00 ppm.

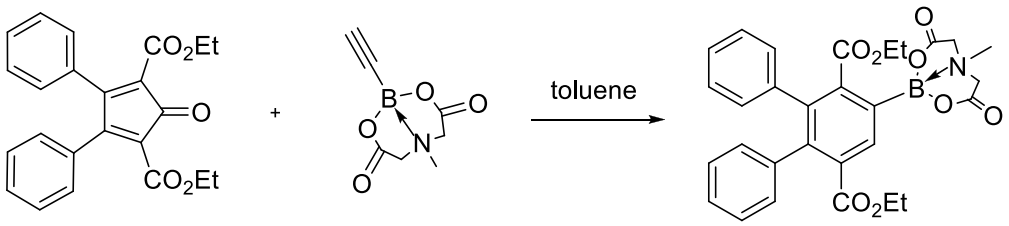
Table 7. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **91**.

Compound	*IR (cm^{-1}) (NaCl plates)*	*^{1}H NMR (δ) ($CDCl_3$)*	*^{13}C NMR (ppm) ($CDCl_3$)*
	3064 (Ar CH) 2993 (Al CH) 1729 (C=O) 1715 (C=O)	1.19 (t, 6H, CH_3) 4.20 (q, 4H, CH_2) 7.03-7.50 (m, 10H, Ar)	13.91, 61.20, 119.82, 127.72, 128.91, 130.14, 131.00, 162.08, 190.96

Ar = aromatic, Al = aliphatic

Synthesis of diethyl 5-hydroxy-2,3-diphenylterephthalate 94

The boronate, diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate **108** was synthesized via Diels-Alder cycloaddition between the cyclopentadienone **91** and ethynyl N-methyliminodiacetic acid (MIDA) boronic ester **89**.



91 **89** **108**

The reaction was run in a pressurized Q-tube with a variety of solvents for varying lengths of time, as shown in **Table 8**, to determine which method was most efficient. It was determined that the reaction produced the highest yields when run for 24 h in toluene at 170°. The product **108** was purified by column chromatography with ethyl acetate/ acetonitrile (95:5); however, purification was not required before oxidization to yield the pure hydroxy terephthalate **94**.

Table 8. Crude Yield of **108** with Varying Time and Solvents.

Solvent	***Time (h)***	***Crude Yield (%)***
Mesitylene	18	34.4
p-Xylene	18	75.2
Toluene	16	77.5
Toluene	24	80.6

The infrared spectrum of the compound **108** exhibited absorptions at 1705, 1726, and 1781 cm^{-1} (**Figures 38** and **Table 9**), the first two of which were attributed to the carbonyl peaks of the ethyl esters and the third attributed to the carbonyl of the MIDA boronate group.

The ^{1}H NMR spectrum of **108** (**Figures 3**, **4**, and **26**) exhibited triplet absorptions at 0.72 (a) and 0.82 δ (f) and quartet absorptions at 3.80 (e) and 3.92 δ (b) corresponding to the six methyl protons and four methylene protons of the ethyl groups on the central ring, respectively. In the aromatic region, absorptions corresponding to ten phenyl group protons were found as a multiplet from 7.00-7.15 δ. The completion of the reaction was confirmed by the singlet absorption at 8.00 δ (j), which corresponds to the single proton on the newly formed benzene ring. A singlet absorption at 3.13 δ (h) and two doublet absorptions at 4.32 (g) and 4.42 δ (g) illustrated in **Figure 3** confirmed the presence of the boronate group.

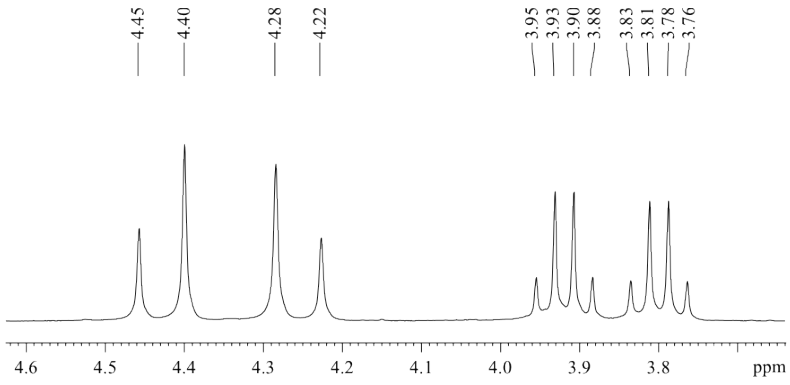


Figure 3. Expanded aliphatic region of the NMR spectrum of **108**.

These peaks were attributed to the methyl and the methylene protons attached to the nitrogen, respectively. The methylene protons (g: H_1 and H_2) of the boronate group were presented as a pair of doublet absorptions (J = 18 Hz) due to geminal coupling between the two magnetically nonequivalent protons on each of the methylene carbons, which is characteristic of MIDA boronates.[33]

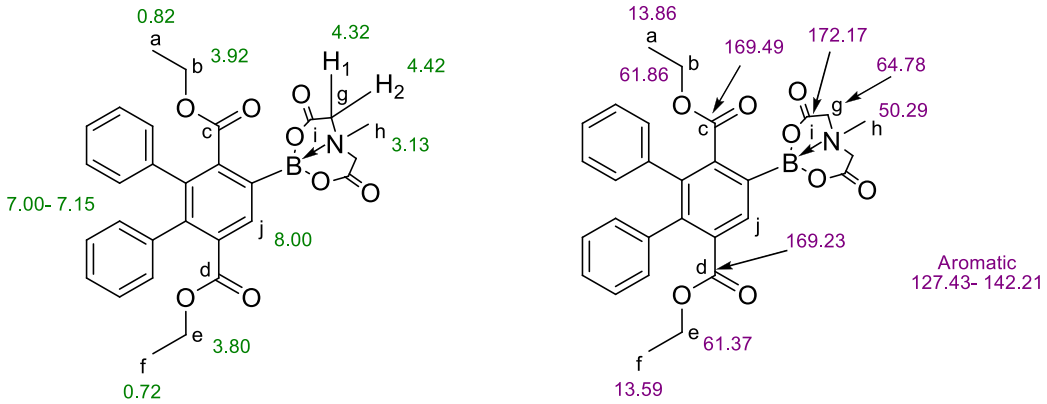
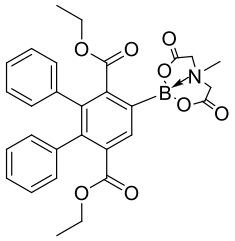


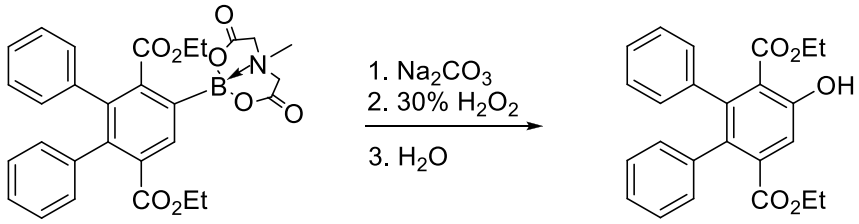
Figure 4. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **108**.

The carbon atoms of the aromatic boronate **108** were identified using ^{13}C NMR spectroscopy (**Figures 4** and **37**). The methyl absorptions associated with the ethyl group were present at 13.59 (f) and 13.86 ppm (a), while the methylene absorptions associated with the ester were present at 61.37 (e) and 61.86 ppm (b). The carbonyl absorptions of the ethyl esters were present at 169.23 (d) and 169.49 ppm (c). The symmetrical boronic acid ester group exhibited a methyl absorption at 50.29 ppm (h), a methylene absorption at 64.78 ppm (g) and an absorption at 172.17 ppm (i) attributed to the carbonyl of the ester. The remaining twelve absorptions ranging from 127.43- 142.21 ppm were attributed the seven primary and five quaternary aromatic carbons of the compound with some absorption overlap, potentially at 134.58 and 142.17 ppm. These assignments were confirmed using DEPT 135.

Table 9. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of boronate **108**.

Compound	*IR (cm^{-1}) (NaCl plates)*	*^{1}H NMR (δ) ($Acetone_6$)*	*^{13}C NMR (ppm) ($Acetone_6$)*
	1705 (C=O) 1726 (C=O) 1781 (C=O of boronate) 2983 (Al, CH)	0.72 (t, 3H, CH_3) 0.82 (t, 3H, CH_3) 3.13 (s, 3H, NCH_3) 3.80 (q, 2H, CH_2) 3.92 (q, 2H, CH_2) 4.32 (d, 2H, NCH_2) 4.42 (d, 2H, NCH_2) 7.00- 7.15(m, 10H, Ar) 8.00 (s, 1H, Ar)	13.59, 13.86, 50.29, 61.37, 61.86, 64.78, 127.43, 127.62, 127.95, 128.03, 130.65, 131.29, 134.19, 134.58, 139.27, 140.02, 142.17, 142.21, 169.23, 169.49, 172.17

The boronate **108**, was hydrolyzed, then oxidized to the corresponding hydroxy compound, diethyl 5-hydroxy-2,3-diphenylterephthalate **94**, in a solution of ethanol, 30% hydrogen peroxide, and sodium carbonate over a period of 3 h at room temperature.



108 **94**

The IR spectrum of compound **94** (**Figures 41** and **Table 10**) exhibited absorptions at 1673 and 1721 cm^{-1} attributed to the carbonyls of the esters. The significantly lower frequency of the carbonyl at 1673 cm^{-1} may be the result of intermolecular hydrogen bonding between the hydroxy proton and C=O (c) of the ester ortho to the hydroxy group.

The conversion of the boronate **89** to the hydroxy compound **94** was confirmed using ^{1}H NMR spectroscopy (**Figures 7** and **39**). Triplet absorptions at 0.67 (r) and 0.92 δ (m) and quartet absorptions at 3.93 (p) and 3.99 δ (k) were attributed to the six methyl

protons and the four methylene protons of the ethyl groups, respectively. A singlet absorption at 7.38 δ (d) was attributed to the single proton on the central benzene ring. The absorptions corresponding to ten aromatic protons from the attached phenyl groups were exhibited as a multiplet in the range of 6.89- 7.11 δ. Finally, a singlet absorption at 10.70 δ was attributed to the proton of the hydroxy group. Phenolic peaks are normally found in the region of 4- 7.5 δ, however it was presumed for this compound, that the peak was shifted downfield as a result of hydrogen bonding between the hydroxy proton and the carbonyl oxygen (i) of the ethyl ester ortho to the OH group.

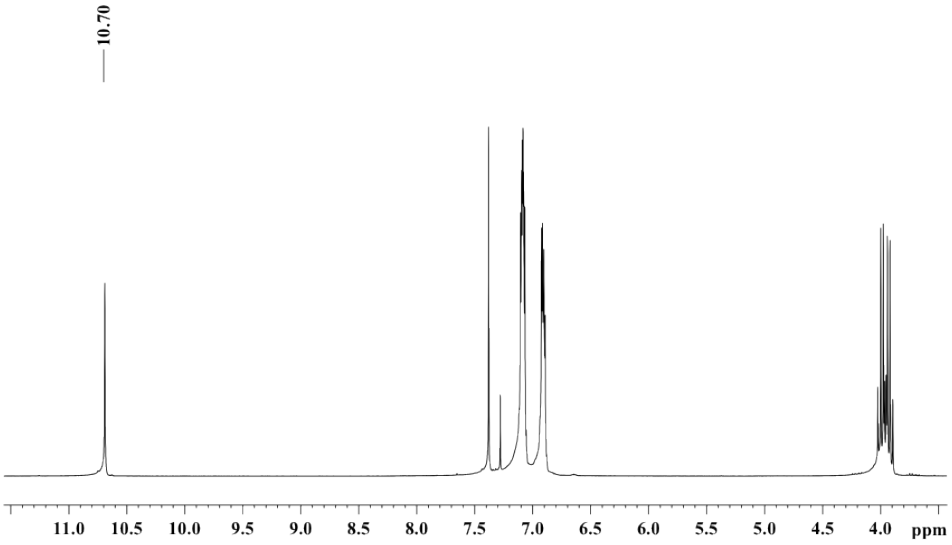


Figure 5. Expanded region of the ^{1}H NMR spectrum of **94**.

This presumption was further verified by analysis of the compound's crystal structure (**Figure 6**). The crystal structure of **94** clearly illustrates the hydrogen bonding that occurs between the carbonyl and the hydroxy proton in the molecule, likely the cause of the downfield shift of the hydroxyl proton absorption in the ^{1}H NMR spectrum.

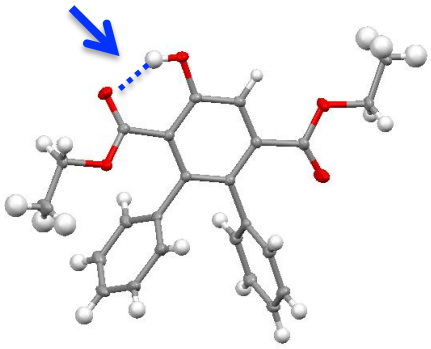


Figure 6. Crystal Structure of **94**.

Analysis of the crystal structure of **94** provided additional information about the structure and packing of the compound. The crystal structure has an orthorhombic lattice (space group, Pbca), plate morphology, and cell parameters a = 6.8762 Å, b = 23.0657 Å, c = 24.7835 Å, α = 90.0°, β = 90.0°, γ = 90.0°, and V = 3930.77 Å^3.

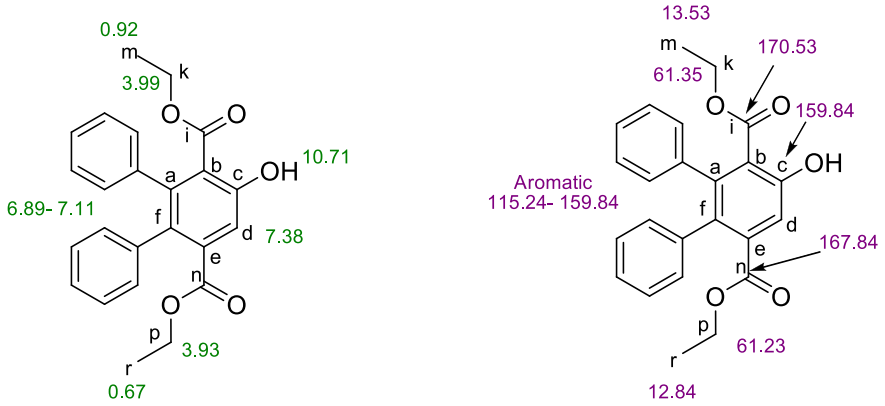
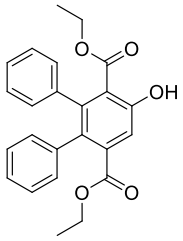


Figure 7. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **94**.

The carbon atoms present in **94** were confirmed using ^{13}C NMR and DEPT 135 spectroscopy (**Figures 7** and **40**). The methyl absorptions of the ethyl groups were present at 12.84 (r) and 13.53 ppm (m), while the methylene absorptions of the ethyl groups were present at 61.23 (p) and 61.35 ppm (k). The carbonyl absorptions of the ethyl esters were present at 167.84 (n) and 170.53 ppm (i). The remaining fourteen

absorptions in the range of 115.24- 159.84 ppm can be associated with the seven primary and seven quaternary aromatic carbon of the compound.

Table 10. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of Hydroxyterephthalate **94**.

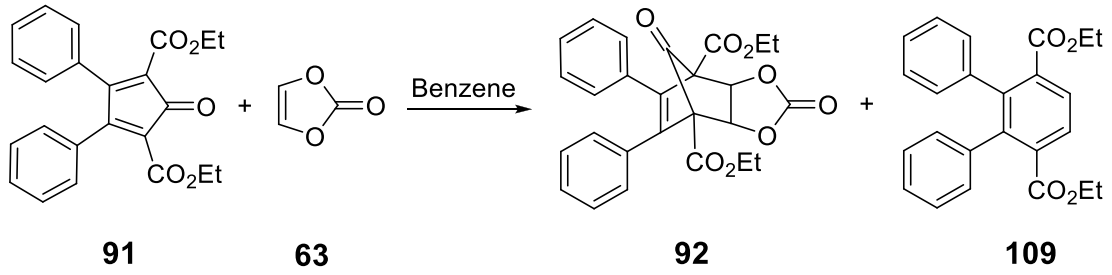
Compound	***IR (cm^{-1}) (NaCl plates)***	***^{1}H NMR (δ) ($CDCl_3$)***	***^{13}C NMR (ppm) ($CDCl_3$)***
	1673 (C=O) 1721 (C=O) 2983 (Al, CH) 3030 (Ar, CH) 3059 (Ar, OH)	0.67 (t, 3H, CH_3) 0.92 (t, 3H, CH_3) 3.93 (q, 2H, CH_2) 3.99 (q, 2H, CH_2) 6.89- 7.11 (m, 10H, Ar) 7.38 (s, 1H, Ar) 10.70 (s, 1H, OH)	12.84, 13.53, 61.23, 61.35, 115.24, 116.87, 126.24, 126.32, 126.90, 127.03, 129.52, 130.34, 132.58, 138.28, 138.62, 140.36, 144.08, 159.84, 167.84, 170.53

The boronic ester was easily synthesized and oxidized to the hydroxy terephthalate in relatively good yields; however, the high cost of the starting material **89** ($175.50/ gram) and poor "atom economy" of the reaction gave rise to a search for an alternative method to synthesize the terephthalate.

A disubstituted hydroxy-phenylated terephthalate was previously synthesized by Harrison in 1979[20] via a Diels-Alder reaction between a cyclopentadienone and vinylene carbonate. A reinvestigation of this procedure was undertaken.

A solution of cyclopentadienone **91** and vinylene carbonate **63** in benzene was heated to 70° in a Q-tube for 24 h to yield a mixture of the bridged adduct, 4,7-bis(carboethoxy)-5,6-diphenyl-3a,7a-dihydrobenzodioxol-2-one, **92** and diethyl 2,3-diphenylterephthalate **109**. The bridged adduct was isolated via recrystallization from benzene/petroleum ether. The reaction was run with varying molar equivalents of vinylene carbonate **63** to determine its impact on reaction yields as illustrated in **Table**

11. As expected overall, the yield of the product **92** increases with increasing molar equivalents of **63**, with the best yield obtained at 1.44 molar eq.



91 **63** **92** **109**

Table 11. Percent Yields of **92** with Varying Molar Equivalents of **63**.

Trial	*Molar eq. Vinylene carbonate*	*% Yield*
1	1.10	60.9
2	1.27	77.3
3	1.32	79.1
4	**1.44**	**82.3**
5	1.46	80.4

The IR spectrum of the bridged adduct **92** exhibited a sharp absorption at 1736 cm[1], attributed to the carbonyl peaks of the esters and carbonate group and a sharp absorption at 1814 cm^{-1}, attributed to the C=O bridge on the central six-membered ring (**Figure 44**, **Table 12**).

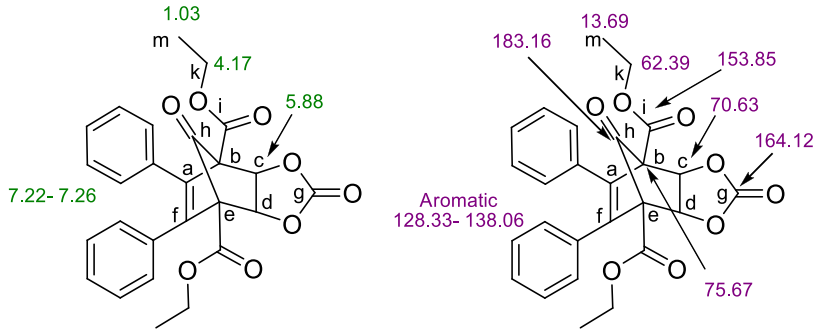


Figure 8. Found [1]H NMR (left) and [13]C NMR Shifts (right) of **92**.

The [1]H NMR spectrum of **92** (**Figures 8** and **42**) exhibited a triplet absorption at 1.03 δ (m) and a quartet absorption at 4.17 δ (k) corresponding to the six methyl protons

and four methylene protons of the ethyl groups, respectively. A singlet at 5.88 δ (c) was attributed to the two methine protons on the ring. In addition, a multiplet from 7.22- 7.26 δ was present as the absorptions corresponding to ten aromatic protons on the phenyl groups attached to the central six-membered ring.

The ^{13}C NMR spectrum of **92** (**Figures 8** and **43**) exhibited a distinct absorption at 183.16 ppm (h), corresponding to the ketone bridging the 1 (e) and 4 (b) positions on the 6 membered ring. In addition, peaks were observed at 153.85 (i) and 164.12 ppm (g) representing the carbonyl carbon absorptions of the esters and carbonate group, respectively. The primary and secondary carbon absorptions of the esters were observed at 13.69 (m) and 62.39 ppm (k), respectively, while the tertiary carbon (c) absorption was observed at 70.63 ppm. The absorption representing the quaternary carbon attached to the ester group was observed at 75.67 ppm (b), the three aromatic carbon and two C=C absorptions were observed between 128.33 and 138.06 ppm.

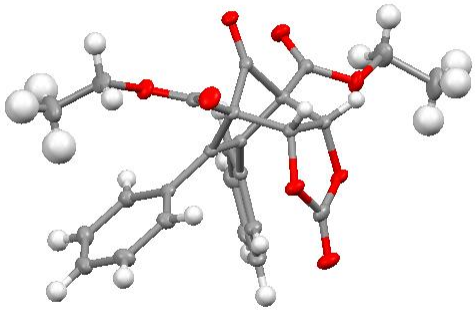
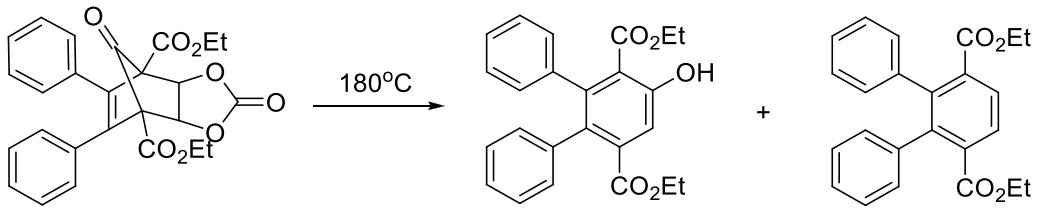


Figure 9. Crystal Structure of **92**.

From the crystal structure data obtained (**Figure 9)**, it was determined that the bridged adduct **92** has an orthorhombic lattice, block morphology, and cell parameters a = 20.0690 Å, b = 7.8142 Å, c = 15.2281 Å, α = 90.0°, β = 109.5383°, γ = 90.0°, and V = 2250.60 Å^3.

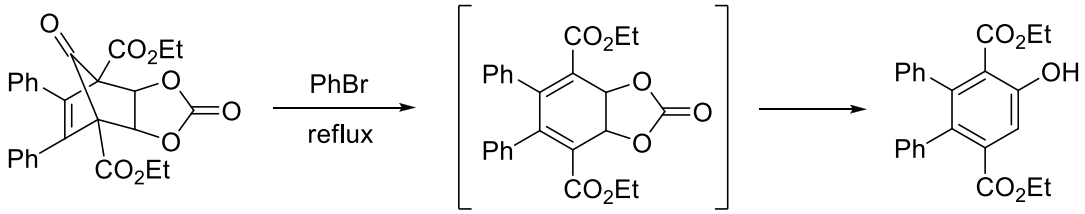
Two approaches were taken to generate the hydroxy terephthalate from **92**. The first involved heating the bridged compound **92** past its melting point of 180° in order for thermal decomposition to occur. The product yielded a mixture of hydroxy phenylated terephthalate **94** and the phenylated terephthalate **109** (**Table 12**), unsubstituted at the 5 position in a ratio of approximately 1:6, respectively. Five separate trials yielded similar results. These compounds were identified using ^{1}H NMR, and ^{13}C NMR (**Figures 45** and **46**, **Table 12**).



92 **94** **109**

The low proportion of hydroxy compound **94** produced relative to **109** and difficulty separating the compounds via column chromatography or phenolic extraction made this method of decarboxylation undesirable and another approach was sought.

The second approach was derived from a method previously used by Harrison to synthesize highly functionalized phenols.[20] The bridged adduct **92** was heated at 150° in bromobenzene. The evolution of the carbonyl bridge produced the cyclohexadiene intermediate **93**. Further heating in bromobenzene caused the evolution of carbon dioxide to the hydroxy-phenylated terephthalate **94**. Reactions were monitored via ^{1}H NMR at 24 h intervals for five to seven days to determine full conversion of **93** to **94**. In cases where the reaction was run above 150° both the bridged adduct **92** and the intermediate **93** underwent thermal decomposition to the phenylated terephthalate, unsubstituted at the 5 position **109**.



92 **93** **94**

The IR spectrum of the intermediate **93** exhibited an absorption at 1651 cm^{-1} that was attributed to the C=C stretching of the cyclohexadiene ring and an absorption at 1713 cm^{-1} (**Figure 50**, **Table 12**) attributed to the C=O of the ester. These absorptions correspond to those observed by Harrison.[24] In addition, the absence of the carbonyl peak at 1814 cm^{-1} confirmed the loss of carbon monoxide upon thermolysis of **92**. The sharp peak at 3402 cm^{-1} was attributed to further decarboxylation of **93** to the hydroxy compound **94**.

The ^{1}H NMR spectrum of **93** (**Figures 10** and **48**) exhibited a triplet absorption at 0.85 δ (m) corresponding to the six methyl protons and a quartet absorption at 3.95 δ (k) corresponding to the four methylene protons of the ethyl groups. A singlet absorption at 6.05 δ (c) represented the two methine protons on each side of the ring's ring fusion carbons. Additionally, absorptions corresponding to ten phenyl group protons were exhibited as a multiplet from 6.83- 7.09 δ.

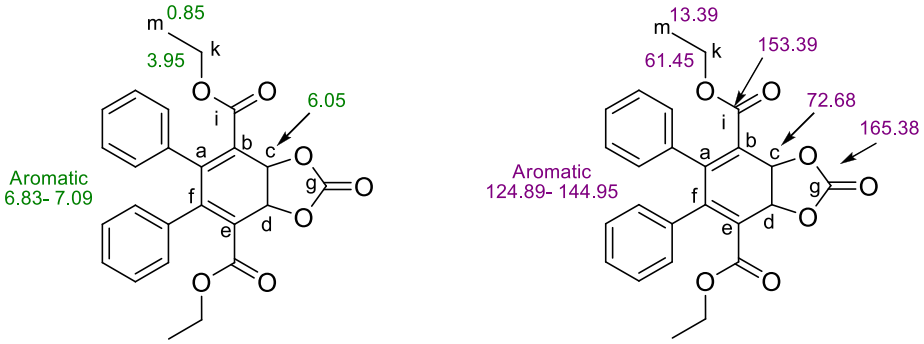


Figure 10. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **93**.

The conversion from the bridged adduct **92** to the intermediate **93** was confirmed with the ^{13}C NMR spectrum of **93 (Figure 49**, **Table 12**) by the absence of the carbonyl bridge absorption (h) at 183.16 ppm as seen in **Figure 11**. Absorptions exhibited at 13.39 (m), 61.45 (k), and 153.39 ppm (i) correspond to the primary, secondary, and carbonyl carbons of the ethyl esters, respectively. The carbonyl carbon of the carbonate group was exhibited as an absorption at 165.38 ppm (g). In addition, an absorption exhibited at 72.68 ppm (c) corresponds to the tertiary carbon of the ring's bridge and six absorptions in the range of 124.89 to 144.95 ppm correspond to the C=C and aromatic carbons of the compound.

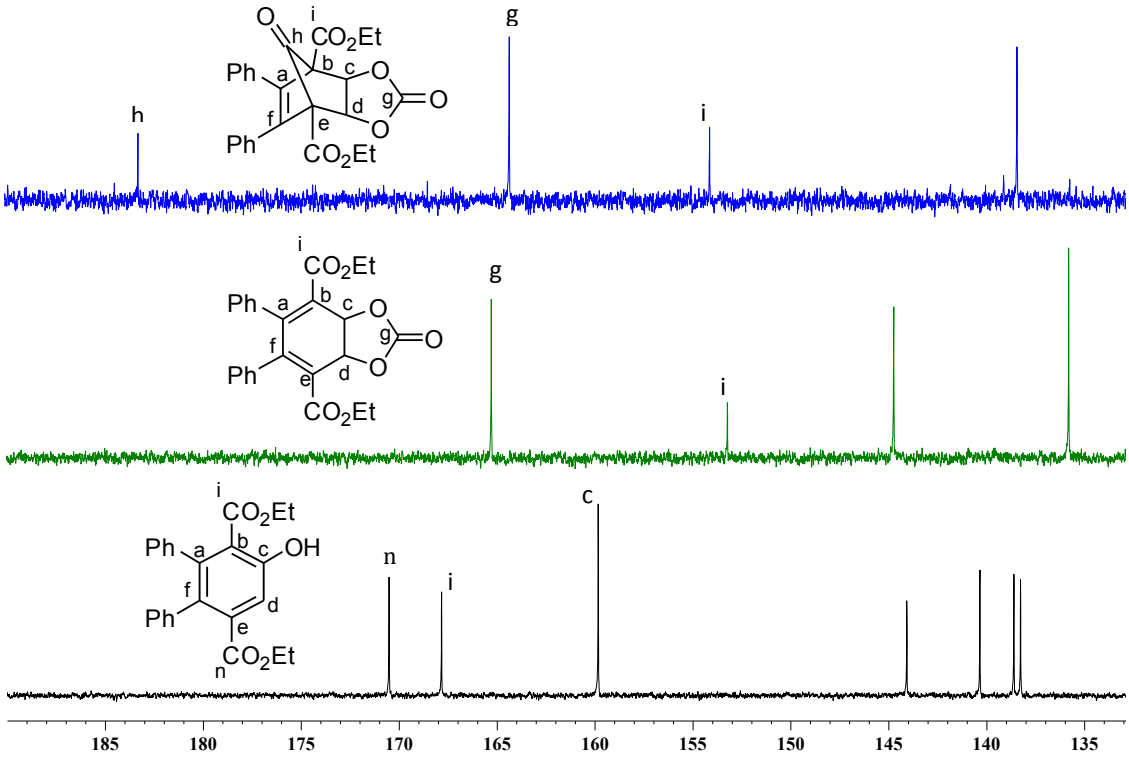
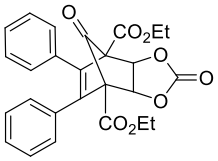
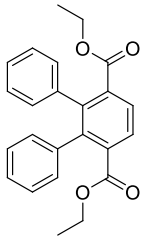
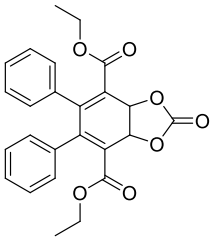
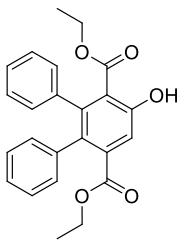


Figure 11. Expanded region of the ^{13}C NMR of **92** (top)**, 93** (middle), and **94** (bottom).

The evolution of carbon dioxide from **93** to yield the hydroxy phenylated terephthalate **94** was also confirmed via ^{13}C NMR. **Figure 11** illustrates the

disappearance of the C=O absorption (g) of the carbonate when **93** is converted to **94**. The unsymmetrical molecule **94**, now has two absorptions (n) and (i) for C=O of the ethyl esters. These peaks are shifted further downfield as a result of the aromatization of the central six-membered ring. Additionally, the aromatization of carbon (c) shifts the absorption from 72.68 to 159.84 ppm.

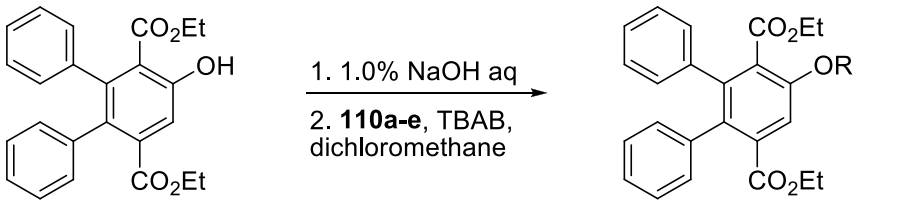
Table 12. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **92**, **109**, **93**, and **94**.

Compound	***IR (cm^{-1}) (NaCl plates)***	***^{1}H NMR (δ) ($CDCl_3$)***	***^{13}C NMR (ppm) ($CDCl_3$)***
	1736 (C=O) 1814 (C=O) 2984 (Al CH)	1.03 (t, 6H, CH_3) 4.17 (q, 4H, CH_2) 5.88 (s, 2H, CH) 7.22-7.26 (m, 10H, Ar)	13.69, 62.39, 70.63, 75.67, 128.33, 128.76, 129.26, 131.88, 138.06, 153.85, 164.12, 183.16,
	-	0.91 (t, 6H, CH_3) 4.01 (q, 4H, CH_2) 6.95- 7.14 (m, 10H, Ar) 7.82 (s, 2H, Ar)	13.53, 61.13, 126.65, 127.19, 127.80, 129.78, 135.36, 138.76, 141.48, 168.31
	1670 (C=C) 1713 (C=O) 2872 (Al CH) 2938 (Al CH) 2985 (Al CH) 3030 (Ar CH) 3061 (Ar CH) 3080 (Ar CH) 3402 (Ar, OH of **1-61**)	0.85 (t, 6H, CH_3) 3.95 (q, 4H, CH_2) 6.05 (s, 2H, CH) 6.83- 7.09 (m, 10H, Ar)	13.39, 61.45, 72.68, 124.89, 127.40, 127.69, 128.50, 136.07, 144.95, 153.39, 165.38
	1724 (C=O) 1773 (C=O) 2903 (Al, CH) 2937 (Al, CH) 2983 (Al, CH) 3024 (Ar, CH) 3058 (Ar, CH) 3400 (Ar, OH)	0.67 (t, 3H, CH_3) 0.92 (t, 3H, CH_3) 3.93 (q, 2H, CH_2) 3.99 (q, 2H, CH_2) 6.89- 7.11 (m, 10H, Ar) 7.38 (s, 1H, Ar) 10.71 (s, 1H, OH)	12.84, 13.53, 61.23, 61.35, 115.24, 116.87, 126.24, 126.32, 126.90, 127.03, 129.52, 130.34, 132.58, 138.28, 138.62, 140.36, 144.08, 159.84, 167.84, 170.53

Though this method was successful in producing the hydroxy-phenylated terephthalate in high yields (95.6%), the high sensitivity of the reagents to thermal decomposition and varying reaction times still makes it a difficult method to reproduce.

Synthesis of Alkoxy-Phenylated Terephthalates

The alkoxy, allyloxy, propargyl, and benzyloxy-phenylated terephthalates were all synthesized via a phase transfer reaction between the hydroxy phenylated



94 **111**

110a, CH_3I
110b, $BrCH_2C{\equiv}CH$
110c, $ClCH_2C_6H_5$
110d, $BrCH_2CCH{=}CH_2$
110e, BrC_4H_9

111a, R= CH_3
111b, R= $CH_2C{\equiv}CH$
111c, R= $CH_2C_6H_5$
111d, $CH_2CCH{=}CH_2$
111e, R= C_4H_9

Table 13. Molar Ratios of Alkyl Halides **110** and Percent Yields of **111**.

Compound	***Alkyl Halide 110***	***Molar Ratio 110: 94***	***Percent Yield (%)***
111a	Iodomethane	3:1	91.1
111b	Propargyl bromide	3:1	74.2
111c	Benzyl chloride	3:1	69.8
111d	Ally bromide	3:1	45.9
111e	Bromobutane	3:1	38.6

terephthalate **94** and the respective alkyl, allyl, propargyl or benzyl halide. Reactions took place in an aqueous sodium hydroxide/ dichloromethane mixture and were catalyzed by tetrabutylammonium bromide. Presented in **Table 13** are the alkyl halides used and the yields obtained from each synthesis.

The infrared spectrum of the methyl ether, diethyl 5-methoxy-2,3-diphenylterephthalate **111a**, exhibited one significant absorption at 1731 cm^{-1} attributed to the carbonyl of the ethyl ester functions (**Figure 53**, **Table 14**).

Methylation of hydroxy compound **94** was confirmed by ^{1}H NMR spectroscopy of the product, **111a** (**Figure 51**). The absence of the hydroxy proton peak at 10.71 δ with the appearance of a singlet at 3.96 δ (h), as illustrated in **Figure 12**, indicates the presence of methoxy protons on the ring. The methyl protons of the ethyl groups exhibited triplet absorptions at 0.86 (g) and 0.90 δ (a), while the methylene protons of the ester exhibited two overlapping quartet absorptions at 3.97 (f) and 4.00 δ (b). In the aromatic region, the ten phenyl group protons exhibited a multiplet absorption from 6.93-7.13 δ and a singlet absorption at 7.38 δ represented the single proton on the main benzene ring.

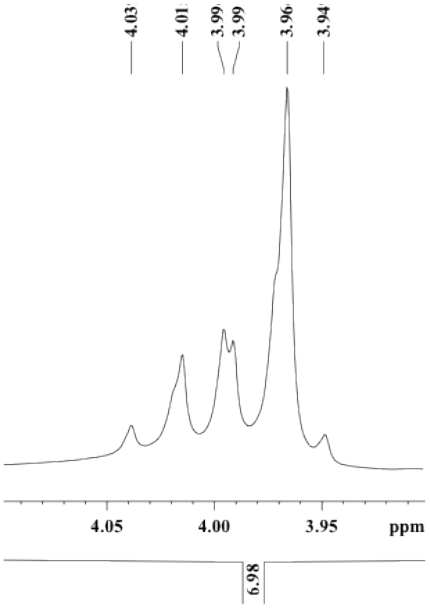


Figure 12. Expanded region of the ^{1}H NMR spectrum of **111a**.

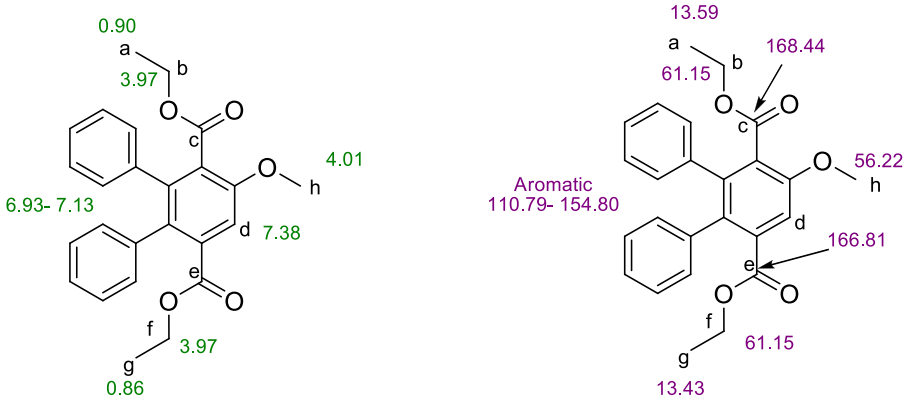


Figure 13. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **111a**.

The carbon atoms present in **111a** were confirmed with ^{13}C NMR (**Figures 13** and **52**) and DEPT 135 spectroscopy. The absorption at 56.22 ppm (h) corresponds to the methoxy carbon. The methyl carbons of the ethyl groups were present as absorptions at 13.43 (g) and 13.59 ppm (a), the methylene carbons of the ethyl group were exhibited as one absorption at 61.15 ppm (b and f), and the carbonyl carbons of the ethyl esters were present as absorptions at 166.81 (e) and 168.44 ppm (c). The eighteen aromatic carbons of the molecule were exhibited as thirteen absorptions in the range of 115.24- 159.84 ppm with two absorptions overlapping.

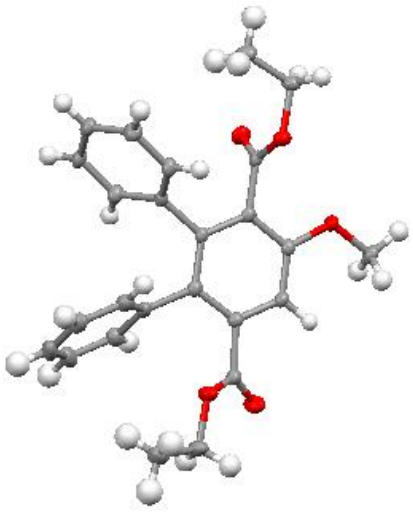


Figure 14. Crystal Structure of **111a**.

The crystal structure analysis of **111a** (**Figure 14)** indicates a monoclinic lattice, block morphology, and cell parameters a = 11.5079Å, b = 6.6345 Å, c = 27.4368 Å, α = 90.0°, β = 94.6202°, γ = 90.0°, and V = 2087.985 Å^3.

The propargyl ether, diethyl 5-propargyloxy-2,3-diphenylbenzenecarboxylate **111b**, exhibited two significant absorptions in the IR spectrum (**Figure 56**, **Table 14**); the first at 1732 cm^{-1}, attributed to the two carbonyl of the ethyl esters functions and the second at 3290 cm^{-1}, attributed to the monosubstituted alkyne of the propargyloxy group.

In the ^{1}H NMR spectrum of **111b** (**Figures 15, 16** and **54**), the terminal proton on the alkyne exhibited a triplet absorption at 2.61 δ (k) due to long range coupling with the methylene protons of (h). Additionally, the methylene protons (h) exhibited a doublet absorption at 4.85 δ. The six methyl protons of the ethyl esters exhibited triplet absorptions at 0.87 (g) and 0.92 δ (a), while the four methylene protons of the ester exhibited quartet absorptions at 3.99 (f) and 4.01 δ (b). In the aromatic region, absorptions corresponding to ten phenyl group protons were exhibited as a multiplet from 6.94- 7.13 δ. A singlet absorption at 7.54 δ (d) corresponds to the single proton on the main benzene ring.

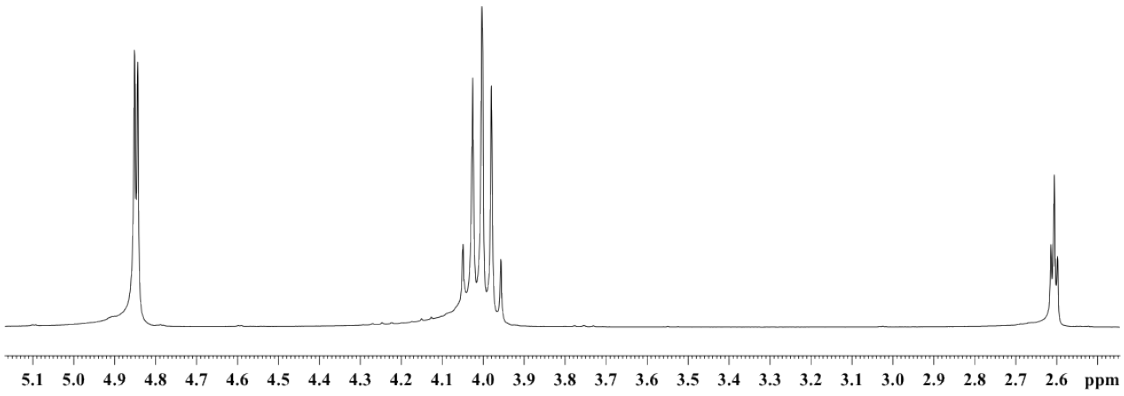


Figure 15. Expanded region of the ^{1}H NMR spectrum of **111b**.

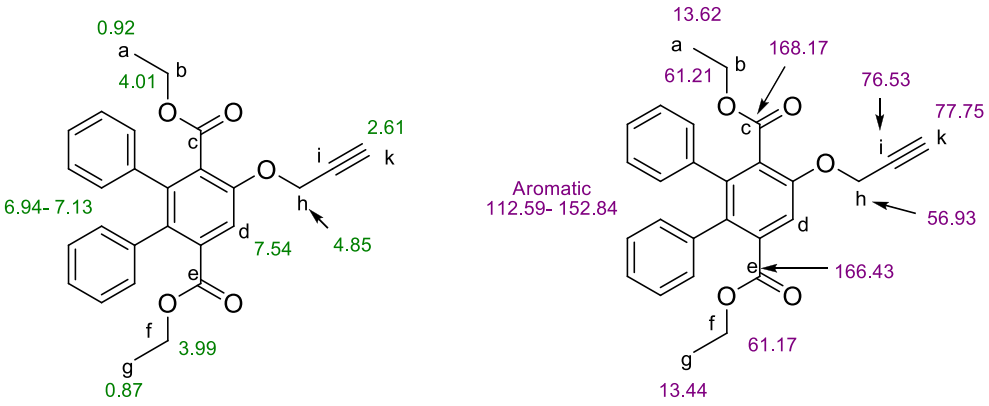


Figure 16. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **111b**.

The ^{13}C NMR spectrum of **111b** (**Figures 16** and **55**) exhibited peaks at 76.53 (i) and 77.75 (k) ppm corresponding to absorptions of the quaternary and terminal carbons of the propargyloxy group respectively, while an absorption at 56.93 ppm (h) corresponds to the methylene carbon attached to the oxygen. The methyl carbons of the ethyl groups exhibited absorptions at 13.44 (g) and 13.62 ppm (a), the methylene carbons of the ethyl group exhibited absorptions at 61.17 (f) and 61.21 ppm (b), and the carbonyl carbons of the ethyl esters exhibited absorptions at 166.43 (e) and 168.17 ppm (c). The remaining fourteen absorptions in the range of 112.59- 152.84 ppm correspond to the eighteen aromatic carbons of the compound.

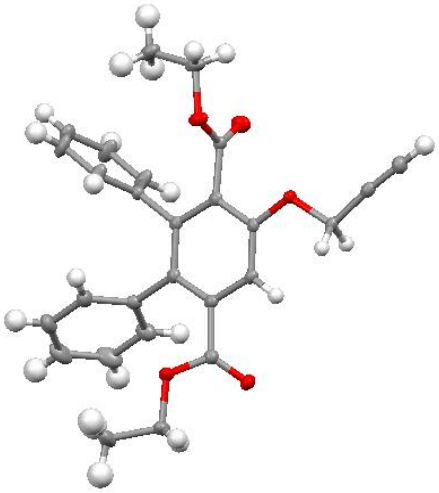


Figure 17. Crystal Structure of **111b**.

The crystal structure of **111b** (**Figure 17**) indicates a monoclinic lattice (space group (2/m(B-unique)), block morphology, and cell parameters a = 23.1319, b = 6.8551 Å, c = 28.2672 Å, α = 90.00°, β = 93.5952°, γ = 90.00°, and V = 4384.30 Å^3.

The benzyl ether, diethyl 5-benzyloxy-2,3-diphenylbenzenecarboxylate **111c**, exhibited one significant IR spectrum peak at 1731 cm^{-1} (**Figure 59**, **Table 14**), which was attributed to the carbonyl of the ethyl ester functions.

The product **111c** was confirmed with ^{1}H NMR spectroscopy (**Figure 18** and **57**). A singlet absorption at 5.26 δ (h) corresponds to the methylene protons of the benzyloxy group. The multiplet absorption ranging from 6.95- 7.49 δ corresponds to the sixteen aromatic protons present in the molecule, ten phenyl group protons (k and m), a single proton on the main ring (d), and five aromatic protons on benzene ring (i) of the benzyloxy group. In addition, the spectrum exhibited triplet absorptions at 0.86 (g) and 0.93 δ (a) and quartet absorptions at 3.98 (f) and 4.03 δ (b) corresponding to the six methyl and four methylene protons of the ethyl groups, respectively.

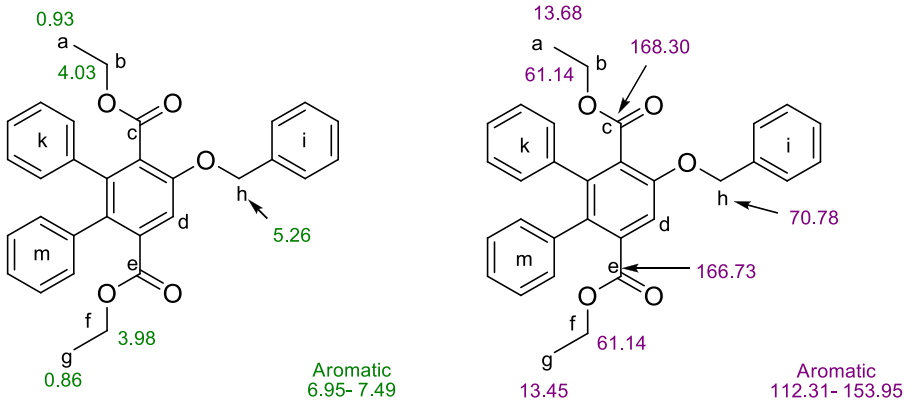


Figure 18. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **111c**.

In the ^{13}C NMR spectrum (**Figures 18** and **58**) of **111c**, the methyl carbon absorptions of the ethyl groups were exhibited at 13.45 (g) and 13.68 ppm (a), the

methylene carbon absorptions of the ethyl groups was exhibited as one peak at 61.14 ppm (b and f), and the carbonyl carbon absorptions of the ethyl esters were exhibited at 166.73 (e) and 168.30 ppm (c). The absorption corresponding to the secondary carbon of the benzyloxy substituent was exhibited at 70.78 ppm (h) and the remaining eighteen aromatic carbons were exhibited as absorptions between 112.31 and 153.95 ppm. These observations were confirmed by DEPT 135 spectroscopy.

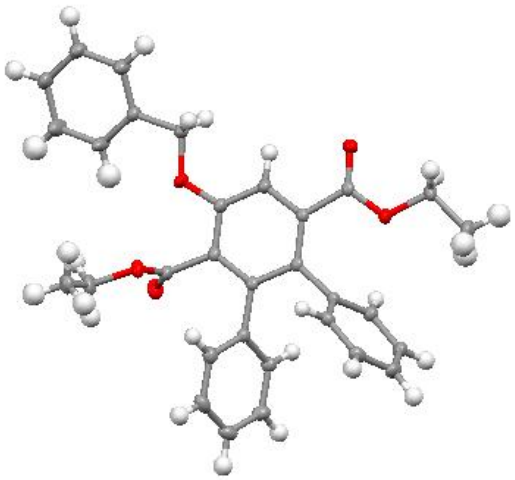


Figure 19. Crystal Structure of **111c.**

The crystal structure of **111c** (**Figure 19**) indicates a triclinic lattice (space group (P-1(2)c)), block morphology, and cell parameters a = 9.5874, b = 11.7383 Å, c = 13.2908 Å, α = 64.1764°, β = 80.1049°, γ = 67.02666°, and V = 1239.2 Å^3.

The allyl ether, diethyl 5-allyloxy-2,3-diphenylterephthalate **111d**, exhibited two significant absorptions in the IR spectrum (**Figure 62 and Table 14**); one at 1648 cm^{-1}, attributed to the C=C stretch and one at 1732 cm^{-1}, attributed to the C=O of the two esters functions.

The ^{1}H NMR spectrum of **111d** (**Figures 20, 21** and **60**) exhibited triplet absorptions at 0.76 (g) and 0.84 δ (a) corresponding to the six methyl protons and quartet

absorptions at 3.95 (f) and 3.94 δ (b) corresponding to the four methylene protons of the ethyl groups, respectively. The allyloxy group on the benzene ring exhibited triplet absorptions at 4.61 (H_1) and 4.63 δ (H_2), attributed to the two magnetically nonequivalent methylene protons on carbon (h). A multiplet absorption present from 6.01- 6.13 δ corresponds to the methine proton (i) on the double bond. Quartet absorptions at 5.22 δ (H_5) and 5.37 δ (H_6), correspond to the two magnetically nonequivalent terminal protons on carbon (k). In addition, a multiplet absorption from 6.83- 7.09 δ corresponds to the ten protons of the phenyl rings and a singlet absorption at 7.27 δ corresponds to the aromatic proton on the main ring.

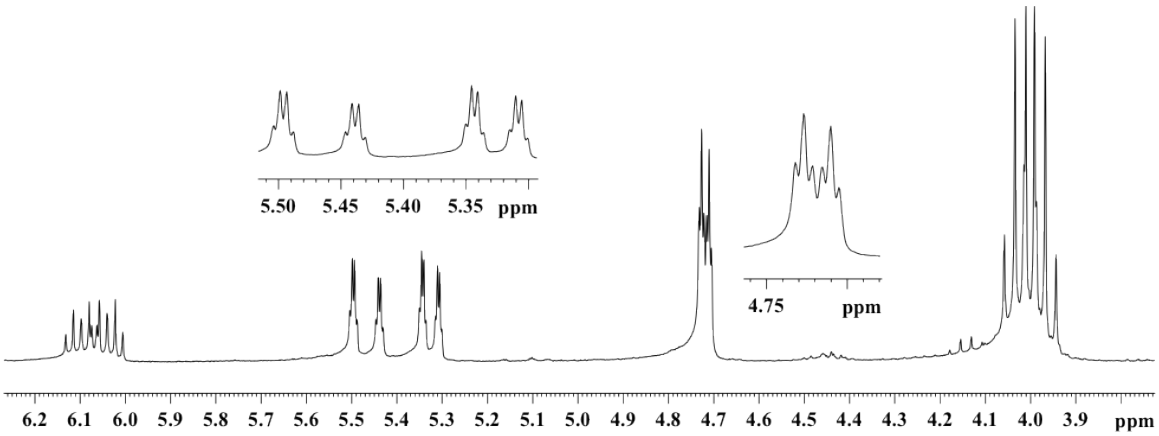


Figure 20. Expanded region of the ^{1}H NMR spectrum of **111d**.

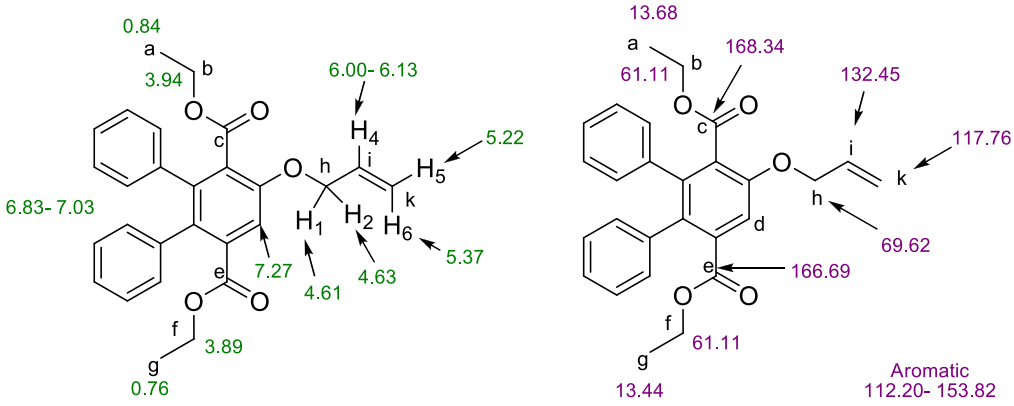


Figure 21. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **111d**.

The carbon atoms of ether **111d** were confirmed using ^{13}C NMR (**Figures 21** and **61**) and DEPT 135 spectroscopy. Absorptions at 69.62 (h), 132.45 (i), and 117.76 ppm (k) correspond to the methylene carbon, methine, and terminal methylene carbons of the alkoxy group respectively. The methyl carbons of the ethyl groups exhibited absorptions at 13.44 (g) and 13.68 ppm (a), the methylene carbons of the ester exhibited one absorption at 61.11 ppm (f and b), and the carbonyl carbons of the ethyl esters exhibited absorptions at 166.69 (e) and 168.34 ppm (c). The remaining fourteen absorptions in the range of 112.20- 153.82 ppm correspond to the aromatic carbons of the compound.

The butoxy ether, Diethyl 5-butoxy-2,3-diphenylterephthalate **111e**, exhibited a significant absorption in the IR spectrum (**Figure 65**, **Table 14**) at 1732 cm^{-1} attributed to the two ester carbonyls of the compound. In addition, sharp absorptions found in the range of 2910- 2982 cm^{-1} were attributed to the aliphatic C-H stretching of the butoxy group.

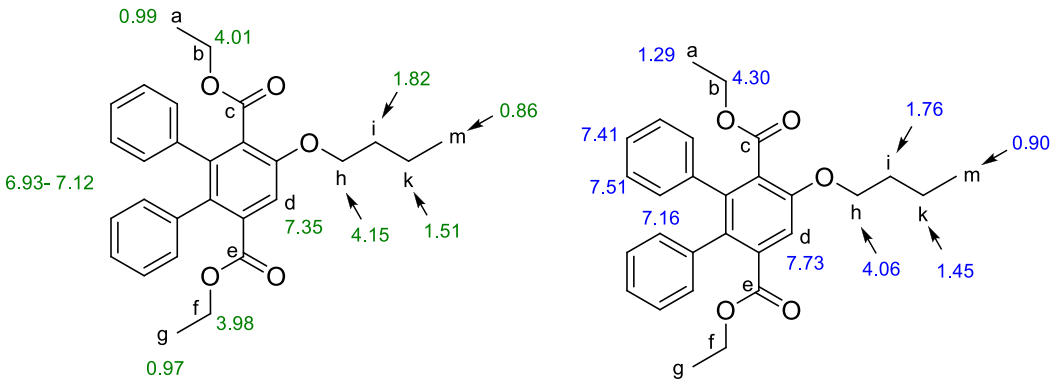


Figure 22. Actual (left) vs. Predicted (right) ^{1}H NMR Shifts for **111e**.

The ^{1}H NMR spectrum of **111e** (**Figure 22**, **23**, and **63**) exhibited triplet absorptions at 0.97 (g) and 0.99 δ (a) corresponding to the six methyl protons and quartet absorptions at 3.98 (f) and 4.01 δ (b) corresponding to the four methylene protons of the ethyl groups. A multiplet absorption ranging from 6.93- 7.12 δ corresponds to the ten

protons of the phenyl rings and a singlet absorption at 7.35 δ (d) corresponds to the aromatic proton on the main ring. The methylene protons on carbon (h) exhibited a triplet absorption at 4.15 δ. The methylene protons on carbon (i) exhibited a quintet absorption at 1.82 δ and the methylene protons on carbon (k) exhibited a sextet absorption at 1.51 δ. Finally the three methyl protons on carbon (m) exhibited a triplet absorption at 0.86 δ. The actual and predicted ^{1}H NMR shifts are illustrated in **Figure 24**.

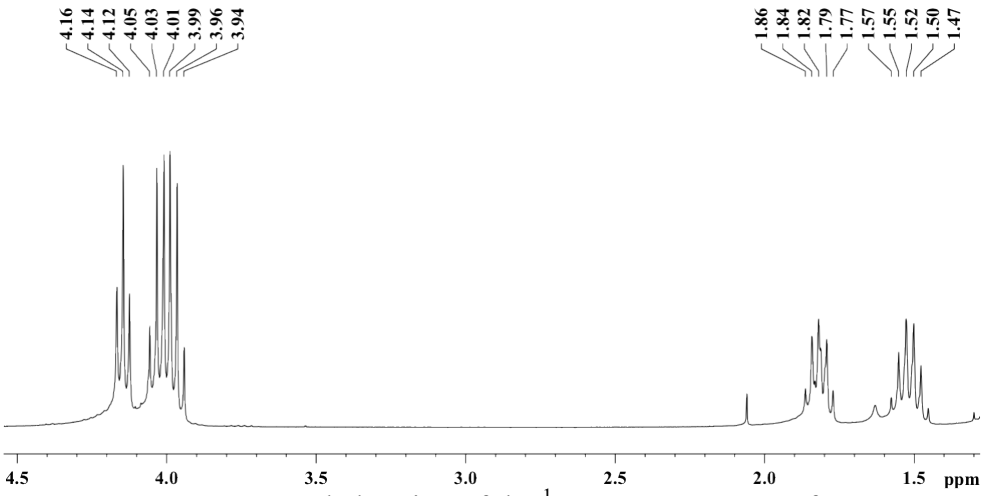


Figure 23. Expanded region of the ^{1}H NMR spectrum of **111e**.

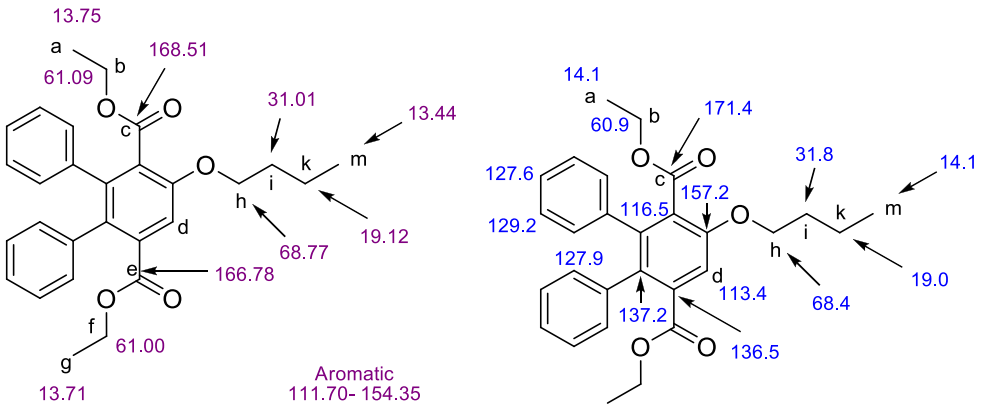
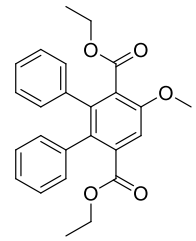
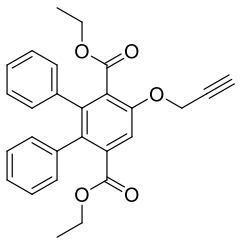


Figure 24. Actual (left) vs. Predicted (right) ^{13}C NMR Shifts for **111e**.

The carbon atoms of the ether **111e** were confirmed using ^{13}C NMR (**Figures 24** and **64**) and DEPT 135 spectroscopy. The absorptions of butoxy carbons (h), (i), (k), and (m) were exhibited at 68.77, 31.07, 19.12, and 13.44 ppm, respectively, as illustrated in

Figure 24. The methyl carbon absorptions of the ethyl groups were exhibited at 13.71 (g) and 13.75 ppm (a), the methylene carbon absorptions of the ester were exhibited at 61.00 (f) and 61.09 ppm (b), and the carbonyl carbon absorptions of the ethyl esters were exhibited at 166.78 (e) and 168.51 ppm (c). The remaining fourteen absorptions in the range of 111.70- 154.35 ppm correspond to the aromatic carbons of the compound.

Table 14. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **111a-e**.

Compound	***IR (cm^{-1}) (NaCl plates)***	***^{1}H NMR (δ) ($CDCl_3$)***	***^{13}C NMR (ppm) ($CDCl_3$)***
	1731 (C=O)	0.86 (t, 3H, CH_3) 0.90 (t, 3H, CH_3) 3.97 (m, 4H, CH_2) 4.01 (s, 3H, CH_3) 6.93- 7.13 (m, 10H, Ar) 7.38 (s, 1H, Ar)	13.43, 13.59, 56.22, 61.15, 110.79, 126.41, 126.99, 127.19, 127.26, 130.01, 130.08, 133.78, 134.53, 137.56, 138.82, 141.01, 154.80, 166.81, 168.44
	1732 (C=O) 2910 (Al CH) 2936 (Al CH) 2982 (Al CH) 3025 (Ar CH) 3058 (Ar CH) 3290(CCH_2)	0.87 (t, 3H, CH_3) 0.92 (t, 3H, CH_3) 2.61 (t, 1H, CH) 3.99 (q, 2H, CH_2) 4.01 (q, 2H, CH_2) 4.85 (d, 2H, OCH_2) 6.94- 7.13 (m, 10H, Ar) 7.54 (s, 1H, Ar)	13.44, 13.62, 56.93, 61.17, 61.21, 76.53, 77.75, 112.59, 126.49, 127.05, 127.21, 127.28, 127.91, 130.00, 130.02, 134.36, 134.74, 137.42, 138.67, 141.22, 152.84, 166.43, 168.17

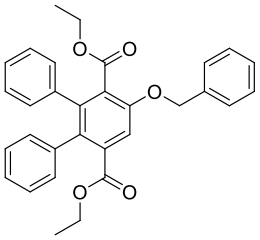
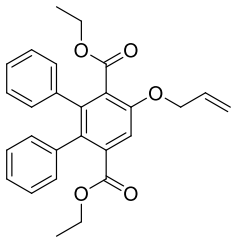
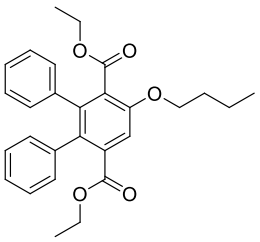
		0.86 (t, 3H, CH_3) 0.93 (t, 3H, CH_3) 3.98 (q, 4H, CH_2) 4.03 (q, 4H, CH_2) 5.26 (s, 2H, OCH_2) 6.95- 7.49 (m, 15H, Ar)	13.45, 13.68, 61.14, 70.78 112.31, 126.43, 127.02, 127.15, 127.21, 127.29, 127.84, 128.01, 128.56, 130.01, 130.07, 134.16, 134.39, 136.32, 137.53, 138.82, 141.09, 153.95, 166.73, 168.30
	1648 (C=C) 1732 (C=O) 2902 (Al CH) 2936 (Al CH) 2982 (Al CH) 3024 (Ar CH) 3058 (Ar CH)	0.76 (t, 3H, CH_3) 0.84 (t, 3H, CH_3) 3.89 (q, 2H, CH_2) 3.94 (q, 2H, CH_2) 4.61 (t, 1H, OCH_2) 4.63 (t, 1H, OCH_2) 5.22 (dd, 1H, CH=C**H**$_2$) 5.37 (dd, 1H, CH=C**H**$_2$) 6.00- 6.13 (m, 1H, C**H**=CH_2) 6.83- 7.03 (m, 10H, Ar) 7.27 (s, 1H, Ar)	13.44, 13.68, 61.11, 69.62, 112.20, 117.76, 126.41, 126.99, 127.19, 127.26, 127.69, 130.01, 130.07, 132.45, 133.96, 134.37, 137.55, 138.83, 141.03, 153.82, 166.69, 168.34
	1732 (C=O) 2873 (Al CH) 2935 (Al CH) 2960 (Al CH) 3025 (Ar CH) 3058 (Ar CH)	0.86 (t, 3H, C**H**$_3$) 0.97 (t, 3H, OCH_2C**H**$_3$) 0.99 (t, 3H, OCH_2C**H**$_3$) 1.51(sextet, 2H, C**H**$_2$$CH_3$) 1.82 (quintet, 2H, CH_2C**H**$_2$$CH_2$) 3.98 (q, 2H, C**H**$_2$) 4.02 (q, 2H, C**H**$_2$) 4.15 (t, 2H, OC**H**$_2$) 6.93- 7.13(m, 10H, Ar) 7.35 (s, 1H, Ar)	13.44, 13.71, 13.75, 19.12, 31.07,60.99, 61.08, 68.77, 111.70, 126.35, 126.94, 127.17, 127.24, 127.53, 130.02, 130.10, 133.53, 134.42, 137.60, 138.93, 140.85, 154.35, 166.78, 168.51

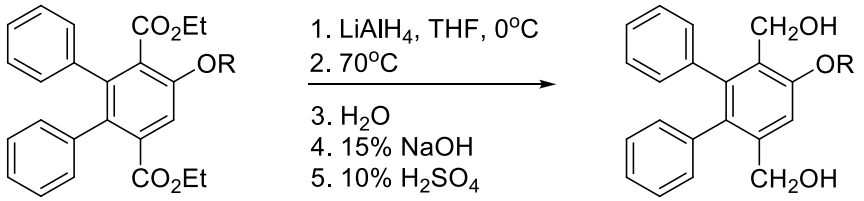
Table 14 cont. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **111a-e**.

Reduction of Alkoxy Phenylated Terepthalate

The alkoxy, allyloxy, propargyloxy, and benzyloxy phenylated terephthalates **111a-d** were reduced to the diols **112a-d** with $LiAlH_4$ in dry THF overnight.

Table 15. Products and Yields of the Reduction of **112**.

Reactant	*Product*	*Percent Yield (%)*
111a	**112a**	94.0
111b	**112b**	40.9
111c	**112c**	77.0
111d	**112b**	47.5



111

111a, R= CH_3
111b, R= $CH_2C{\equiv}CH$
111c, R= $CH_2C_6H_5$
111d, $CH_2CCH{=}CH_2$

112

112a, R= CH_3
112b, R= OH
112c, R= $CH_2C_6H_5$
112b, R= OH

The ^{1}H NMR spectrum of the methoxy diol, 5-methoxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene **112a**, confirmed complete reduction of the terephthalate (**Figures 25**, **26**, **66** and **Table 14**). A singlet absorption exhibited at 3.89 δ (g) corresponds to the methyl protons of the methoxy group. Overlapping doublet absorptions at 4.14 (e) and 4.16 δ (b) correspond to the four methylene protons of the hydroxymethyl groups. Triplet absorptions at 4.28 (f) and 5.11 δ (a) correspond to the two hydroxyl proton of the hydroxymethyl groups. The difference in chemical shifts between proton (f) and proton (a) is most likely due to hydrogen bonding between proton (a) and the oxygen of the methoxy group. The ten phenyl protons were exhibited as a multiplet absorption ranging from 6.89- 7.14 δ and the single aromatic proton on the main ring was exhibited as a single absorption at 7.33 δ.

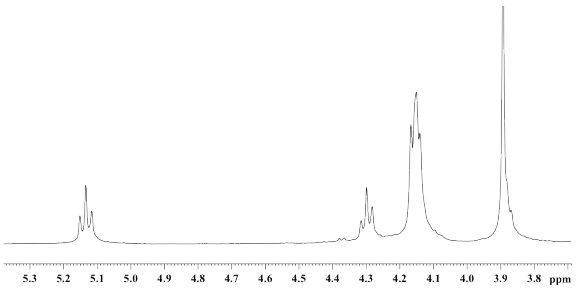


Figure 25. Expanded region of the ^{1}H NMR spectrum of **112a**.

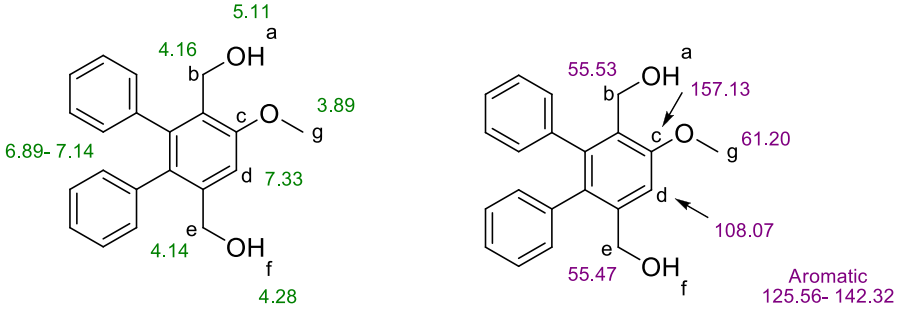


Figure 26. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **112a**.

The ^{13}C NMR spectrum of the methoxy diol **112a** (**Figure 67**) exhibited carbon absorptions for the hydroxymethyl substituents at 55.47 ppm (e) and 55.53 (b) and a methoxy carbon absorption at 61.20 ppm (g). Aromatic absorptions at 108.07 (d) and 157.13 ppm (c) correspond to the primary carbon and quaternary carbon bonded to the oxygen on main benzene ring, respectively. The remaining fourteen absorptions ranging from 125.56 to 142.32 ppm correspond to the aromatic carbons of the molecule with two overlapping carbon absorptions.

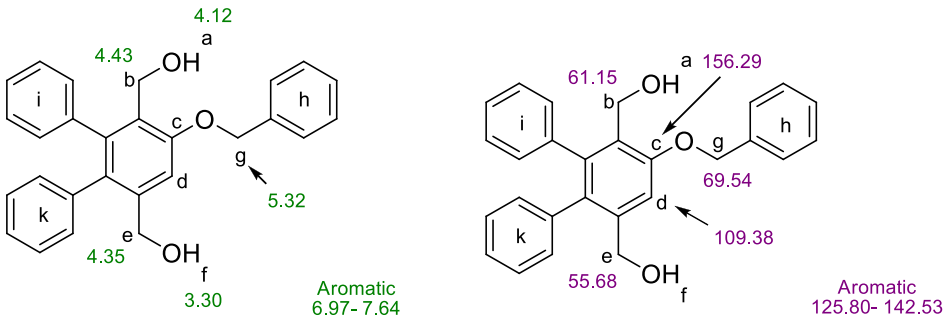


Figure 27. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **112c**.

The ^{1}H NMR spectrum of the benzyloxy ether, 5-benzyloxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene **112c**, confirmed complete reduction of the terephthalate (**Figures 27, 28**, **71** and **Table 14**). A singlet absorption exhibited at 5.32 δ (g) corresponds to the methylene protons of the benzyloxy group. Two doublet absorptions at 4.35 (e) and 4.43 δ (b) and two triplet absorptions at 3.30 (f) and 4.12 δ (a) correspond to the four methylene protons and the two hydroxyl proton of the hydroxymethyl groups, respectively. The downfield shift of proton (a), like that in **112a**, is most likely the result of hydrogen bonding between the proton and the oxygen of the benzyloxy group. The fifteen phenyl protons were exhibited as a multiplet absorption from 6.97- 7.64 δ.

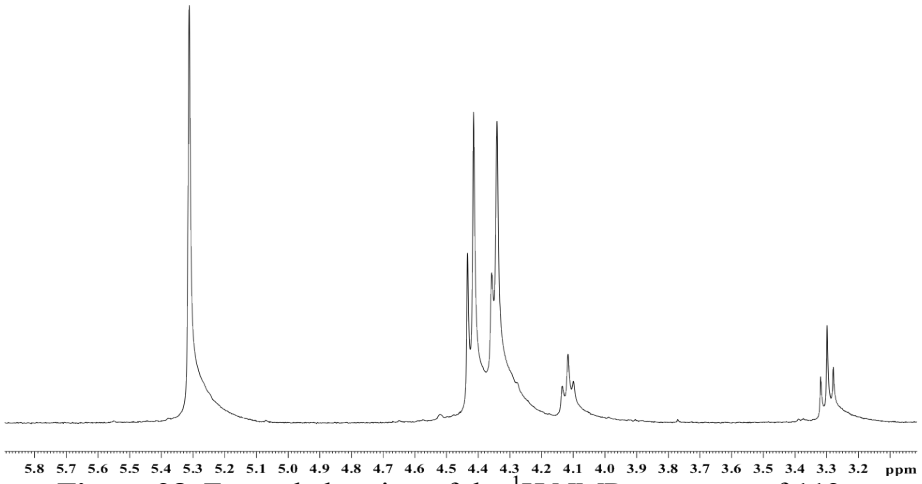


Figure 28. Expanded region of the ^{1}H NMR spectrum of **112c**.

The ^{13}C NMR spectrum of the benzyloxy diol **112c** (**Figure 27** and **72**) exhibited methylene carbon absorptions for the hydroxymethyl groups at 55.68 (e) and 61.15 ppm (a) and a methylene carbon absorption for the benzyloxy group at 69.54 ppm (g). Aromatic absorptions at 109.38 (d) and 156.29 ppm (c) correspond to the primary carbon and quaternary carbon bonded to the oxygen on main benzene ring, respectively. The

remaining sixteen absorptions ranging from 125.80 to 142.53 ppm correspond to the aromatic carbons of the molecule with overlapping of carbon absorptions.

Reduction of both the propargyl terephthalate **111b** and the allyloxy terephthalate **111d** resulted in the formation of the 5-hydoxy-1,4-di(hydroxymethyl)-3,4-diphenylbenzene **112b** (scheme on page 65) as confirmed by ^{1}H NMR spectroscopy (**Figure 29, 30, 68**, and **Table 16**). The ^{1}H NMR spectrum of **112b**, confirmed complete reduction of the terephthalate (**Figures 27, 28**, **68**, **69**, and **Table 14**). A doublet absorptions at 4.09 (e) and a singlet absorption at 4.19 δ (b) correspond to the four methylene protons of the hydroxymethyl group. A broad singlet absorption at 4.53 (f) and a triplet absorption at

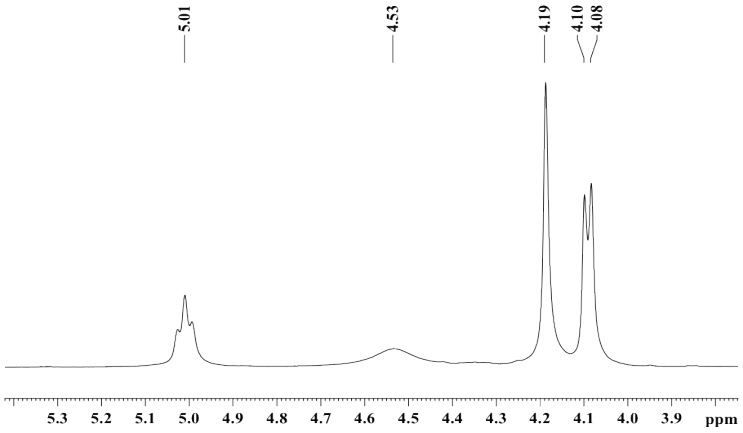


Figure 29. Expanded region of the ^{1}H NMR spectrum of **112d**.

5.01 δ (a) correspond to the two hydroxyl proton of the hydroxymethyl groups. The eleven phenyl protons exhibited a multiplet absorption ranging from 6.87- 7.14 δ. The broad absorption exhibited at 9.52 δ corresponds to the proton of the hydroxy group (g). In addition, the absence of the allyl group absorptions in the range of 0.76- 6.03 δ and the propargyl group absorptions at 2.61 and 4.85 δ, indicated that in both cases the group on the oxygen was removed in the reaction.

The ^{13}C NMR spectrum of the hydroxy diol **112b** (**Figure 70**) exhibited two methylene carbon absorptions for the hydroxymethyl substituents at 56.71 (e) and 61.05 ppm (a). Aromatic absorptions at 112.49 (d) and 155.42 ppm (c) correspond to the primary carbon and quaternary carbon bonded to the oxygen on main benzene ring, respectively. The remaining twelve absorptions ranging from 123.32 to 141.81 ppm correspond to the aromatic carbons of the molecule.

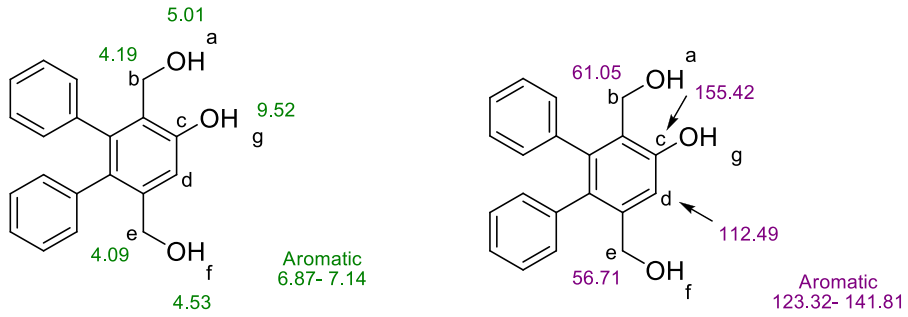
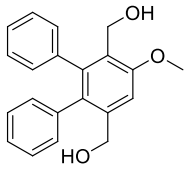
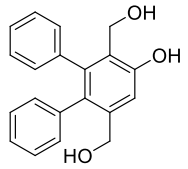
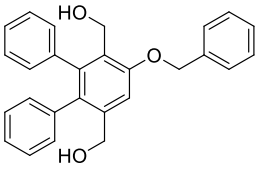


Figure 30. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **112b**.

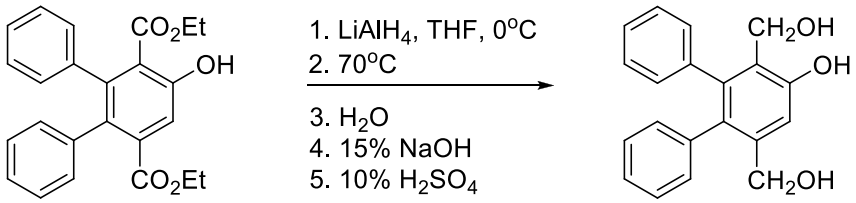
The reduction of **111a** and **111c** produced the corresponding dihydroxymethylbenzenes in good to high yields (77.0-94.0%) as expected (**Table 16**). The reduction of **111b** and **111d** however, provided the hydroxy (dihydroxymethyl)benzene **112b** (**Figure 69**) in low yields (40.9-47.5%) This may be the result of lithium aluminum hydride, already in excess (6 molar eq.), being used up during the reduction of the ether and not enough reducing agent remaining to fully reduce the terephthalate. Increasing the molar equivalence of lithium aluminum hydride used could potentially give purer products in higher yields.

Table 16. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **112a, c,** and **d**.

Compound	*^{1}H NMR (δ) (DMSO)*		*^{13}C NMR (ppm) (DMSO)*
	3.89 (s, 3H, CH_3) 4.14 (d, 2H, CH_2) 4.16 (d, 2H, CH_2) 4.28 (t, 1H, OH) 5.11 (t, 1H, OH) 6.89-7.14 (m, 10H, Ar) 7.33 (s, 1H, Ar)		55.48, 55.53, 61.21, 108.07, 125.56, 125.95, 125.98, 126.82, 127.29, 130.21, 131.27, 139.03, 139.05, 140.55, 142.32, 157.13
	4.09 (d, 2H, C**H**$_2$OH) 4.19 (s, 2H, C**H**$_2$OH) 4.53 (s, 1H, CH_2O**H**) 5.01 (t, 1H, CH_2O**H**) 6.87-7.14 (m, 11H, Ar) 9.52 (s, 1H, O**H**)		56.71, 61.05 112.49, 123.32 125.78, 125.88 126.85, 127.23 129.89, 130.16 130.34, 139.30 139.35, 140.25 141.81, 155.42
Compound	***IR (cm^{-1}) (NaCl plates)***	***^{1}H NMR (δ) (Acetone$_6$)***	***^{13}C NMR (ppm) (DMSO)***
	2341 2359 3309 (Al OH)	3.30 (t, 1H, CH_2O**H**) 4.12 (t, 1H, CH_2O**H**) 4.35 (d, 2H, C**H**$_2$OH) 4.43 (d, 2H, C**H**$_2$ OH) 5.32 (s, 2H, CH_2) 6.97-7.64 (m, 11H, Ar)	55.68, 61.15, 69.54, 109.38, 125.80, 126.06, 126.88, 127.27, 127.33, 127.76, 128.40, 130.16, 131.61, 137.45, 138.90, 138.96, 140.49, 142.53, 156.29

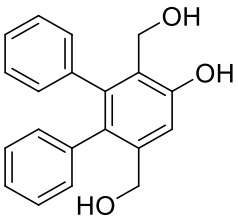
Reduction of diethyl 5-hydroxy-2,3-diphenylterephthalate 94

The hydroxy, phenylated terepthalate **94** was also reduced with lithium aluminum hydride in order to obtain **112b**. The ^{1}H NMR and ^{13}C NMR data coincided with the previous data obtained to within 0.05 ppm as illustrated in **Table 17**. This compound could potentially undergo alkylation of the oxygen to put on side groups, such as allyl and propargyl.



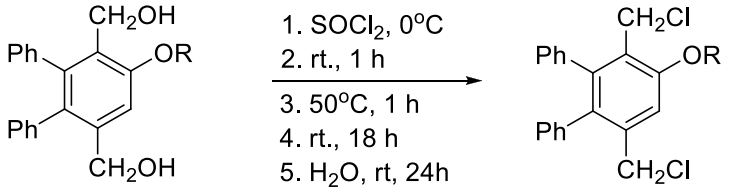
94 **112b**

Table 17. IR, ^{1}H NMR, and ^{13}C NMR Spectral Data of **112b** from **94**

Compound	*^{1}H NMR (δ) (DMSO)*	*^{13}C NMR (ppm) (DMSO)*
	4.09 (s, 2H, C**H**$_2$OH) 4.19 (s, 2H, C**H**$_2$OH) 4.63 (broad s, 1H, CH$_2$O**H**) 5.02 (s, 1H, CH$_2$O**H**) 6.87- 7.14 (m, 11H, Ar) 9.49 (broad s, 1H, OH)	56.73, 61.05, 112.50, 123.32, 125.78, 125.88, 126.85, 127.23, 129.90, 130.16, 130.34, 139.30, 139.35, 140.25, 141.81, 155.42

Chlorination of Alkoxy di(hydroxymethyl)-3,4-diphenylbenzenes

The di(hydroxymethyl)benzenes **112a** and **c** were reacted with thionyl chloride at room temperature overnight to yield the respective di(chloromethyl)benzenes **113a** and **113c**.



112 **113**

112a, R= CH_3
112c, R= $CH_2C_6H_5$

113a, R= CH_3
113c, R= $CH_2C_6H_5$

Table 18. Products and Yields of the Chlorination of **112**.

Reactant	*Product*	*Percent Yield (%)*
112a	**113a**	94.0
112c	**113c**	36.2

The IR spectrum of **113a**, 5-Methoxy-1,4-di(chloromethyl)-3,4-diphenylbenzene (**Figure 75**) exhibited absorptions in the range of 2839- 2963 cm^{-1} attributed to the aliphatic C-H stretching and absorptions in the range of 3023-3056 cm^{-1} attributed to aromatic C-H stretching of the molecule.

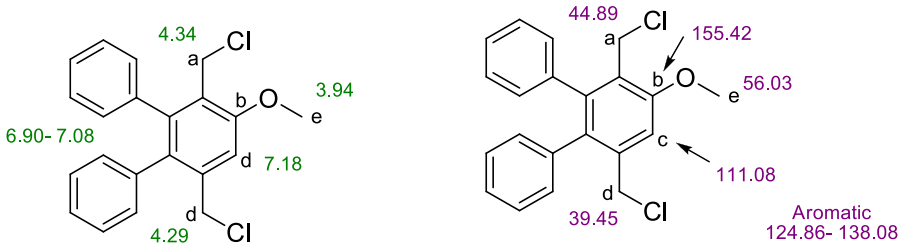


Figure 31. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **113b**.

The conversion to the di(chloromethyl)benzene **113a** was confirmed by ^{1}H NMR spectroscopy (**Figures 73**, **31** and **Table 19)**. A singlet absorption exhibited at 3.94 δ (e) corresponds to the methyl protons of the methoxy group. Two singlet absorptions at 4.29 (d) and 4.34 δ (a) correspond to the four methylene protons of the chloromethyl groups. The ten phenyl proton exhibited a multiplet absorption ranging from 6.90- 7.08 δ and the single aromatic proton on the main ring was exhibited at 7.18 δ.

The ^{13}C NMR specrum of **113a** (**Figure 74**) exhibited two methylene carbon absorptions for the chloromethyl substituents at 39.45 ppm (d) and 44.89 (a) and a methoxy carbon absorption at 56.03 ppm (e). Aromatic absorptions at 111.08 (c) and 155.42 ppm (b) were attributed to the primary carbon and quaternary carbon bonded to the oxygen on main benzene ring, respectively. The remaining eleven absorptions ranging from 124.86 to 138.08 ppm were attributed to the sixteen aromatic carbons of the molecule with possible overlapping of carbon absorptions.

The IR spectrum of **113c** (**Figure 78**), 5-Benzyloxy-1,4-di(chloromethyl)-3,4-diphenylbenzene exhibited absorptions in the range of 2868 to 2976 cm^{-1} attributed to aliphatic C-H stretching and two absorptions at 3029 and 3058 cm^{-1} attributed to the aromatic C-H stretching of the molecule.

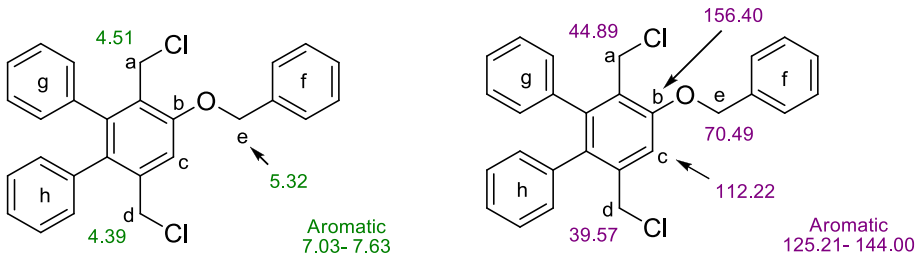
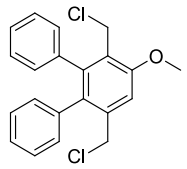
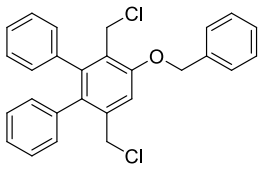


Figure 32. Found ^{1}H NMR (left) and ^{13}C NMR Shifts (right) of **113c**.

The conversion to the di(chloromethyl)benzene **113c** was confirmed by ^{1}H NMR spectroscopy (**Figures 32** and **76**,**Table 19)**. A singlet absorption exhibited at 5.32 δ (e) was attributed to the methylene protons of the benzyloxy group. Two singlet absorptions at 4.39 (d) and 4.51 δ (a) corresponding to the four methylene protons of the chloromethyl groups. The sixteen phenyl proton exhibited a multiplet absorption ranging from 7.03- 7.63 δ.

The ^{13}C NMR spectrum of **113c** (**Figure 77**) exhibited two methylene carbon absorptions for the chloromethyl substituents at 39.57 ppm (d) and 44.89 (a) and a methylene carbon absorption for the benzyloxy group at 56.03 ppm (e). Aromatic absorptions at 112.22 (c) and 156.40 ppm (b) were attributed to the primary carbon and quaternary carbon bonded to the oxygen on main benzene ring, respectively. The remaining fifteen absorptions ranging from 125.21 to 144.00 ppm were attributed to eighteen the aromatic carbons of the molecule with overlapping of carbon absorptions.

Table 19. ^{1}H NMR, and ^{13}C NMR Spectral Data of **113a** and **c**.

Compound	*IR (cm^{-1}) (NaCl plates)*	*^{1}H NMR (δ) ($CDCl_3$)*	*^{13}C NMR (ppm) ($CDCl_3$)*
	1329 (CH_2Cl) 2839 (Al CH) 2937 (Al CH) 2963 (Al CH) 3023 (Ar CH) 3056 (Ar CH)	3.94 (s, 3H, CH_3) 4.29 (s, 2H, CH_2) 4.34 (s, 2H, CH_2) 6.90-7.08 (m, 10H, Ar) 7.18 (s, 1H, Ar)	39.45, 44.89, 56.03, 111.08, 124.86, 126.70, 126.86, 127.41, 127.54, 130.18, 130.54, 134.32, 137.19, 138.08, 143.94, 157.29,
	2868 (Al CH) 2930 (Al CH) 2976 (Al CH) 3029 (Ar CH) 3058 (Ar CH)	4.39 (s, 2H, C**H**$_2$Cl) 4.51 (s, 2H, C**H**$_2$Cl) 5.32 (s, 2H, CH_2) 7.03- 7.63 (m, 15H, Ar)	39.57, 44.89 70.49, 112.22 125.21, 126.73 126.90, 127.31 127.45, 127.56 128.06, 128.68 130.02, 130.52 134.52, 136.68 137.16, 138.06 144.00, 156.40

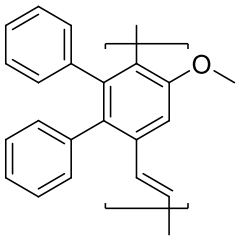
Polymerization of di(chloromethyl)-3,4-diphenylbenzenes

The monomer precursor, 5-methoxy-1,4-di(chloromethyl)-2,3-diphenylbenzene **113a** was polymerized in dry THF with 1.48 eq. 4-*t*-butylbenzyl chloride and 1.0 M potassium t-butoxide. Approximately 10 minutes after warming the solution to room temperature a yellow gel formed. The gel was precipitated in methanol, filtered and air-dried to yield an insoluble orange solid. Thermogravimetric analysis of the polymer showed 5% weight loss at 381.47° (**Figure 80)**. Differential scanning calorimetry gave a glass transition temperature of 125.94° (**Figure 81)**.

The IR spectrum of poly(5-methoxy-1,4-phenylene vinylene) **114a** (**Figure 79**, **Table 20**) exhibited an absorption at 1601 cm^{-1} attributed to C=C stretching, absorptions

at 2834, 2934, 2994 cm^{-1} attributed to aliphatic C-H stretching, and absorptions at 3022 and 3058 cm^{-1} attributed to the aromatic C-H stretching of the molecule.

Table 20. IR Spectral Data of **114a**.

Compound	*IR (cm^{-1}) (NaCl plates)*
	1601 (C=C) 2834 (Al, CH) 2934 (Al, CH) 2994 (Al, CH) 3022 (Ar, CH) 3055 (Ar, CH)

Conclusions

- Ethynyl MIDA boronate **89** was successfully used in the synthesis of the corresponding boronated terephthalate **109**, which could be conveniently converted to the hydroxy terephthalate **94** in high yield.
- The high cost of the starting material **89** and poor "atom economy" of the reaction made this method of synthesizing hydroxy terephthalate **94** undesirable.
- Reinvestigation into the synthesis of the dihydrobenzodioxolone **92** using vinylene carbonate resulted in isolation of the product in high yield.
- The dihydrobenzodioxolone **92** underwent two decarboxylation reactions:
    - Melting to produce a mixture of the hydroxy **94** and unsubstituted at the 5 position.
    - Refluxing in bromobenzene to produce the cyclohexadiene **93,** then **94**.
    - The high sensitivity of the reagents to thermal decomposition and varying reaction times made this method difficult to reproduce.
- Methoxy, propargyloxy, benzyloxy, allyloxy, and butoxy terephthalates were synthesized via a phase transfer reaction in yields ranging from 38.6- 91.1%.
- Methoxy and benzyloxy terepthalate could be reduced to the corresponding di(hydroxylmethyl)benzenes.
- Allyloxy and propargyloxy terepthalate could be reduced to the corresponding 5-hydroxy1.4-di(hydroxylmethyl)benzene **112b**.
- Hydroxy terephthalate **94** was reduced to **112b** yield of 48.4%.
- Methoxy and benzyloxy di(hydroxymethyl)benzenes were converted to the corresponding di(chloromethyl)benzenes.
- Methoxy di(hydroxymethyl)benzene was polymerized to yield a bright-orange insoluble polymer.

Future Work

- Develop alternative methods to synthesize the hydroxy terephthalate **94**, possibly using cheaper, easier to synthesize ethynyl boronates.
- Incorporate larger alkoxy side groups into the terephthalate via a phase transfer reaction.
- Employ different reduction methods to prevent cleavage of R groups on oxygen in the hydroxy terephthalates.
- Develop a method to alkylate hydroxy di(hydroxymethyl)benzene and subsequently convert the products to the corresponding alkoxy di(cholоromethyl)benzene monomers.
- Develop polymerization of alkoxy di(chloromethyl)benzene monomers.

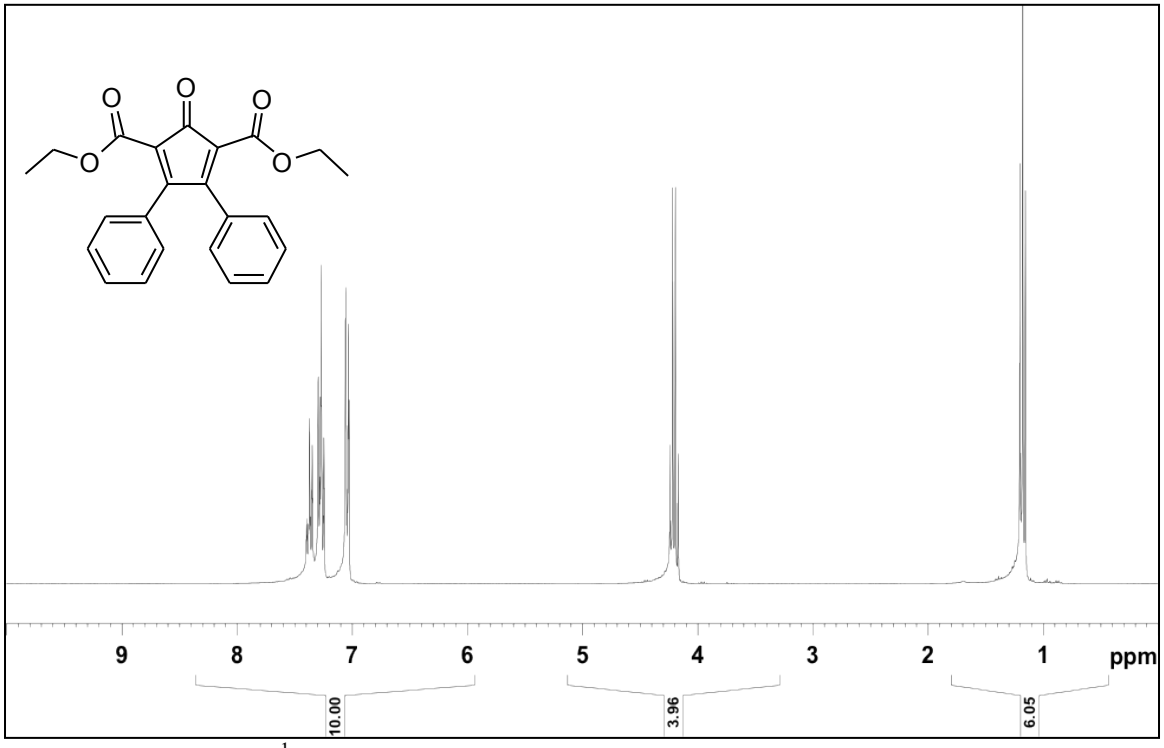


Figure 33: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **91**.

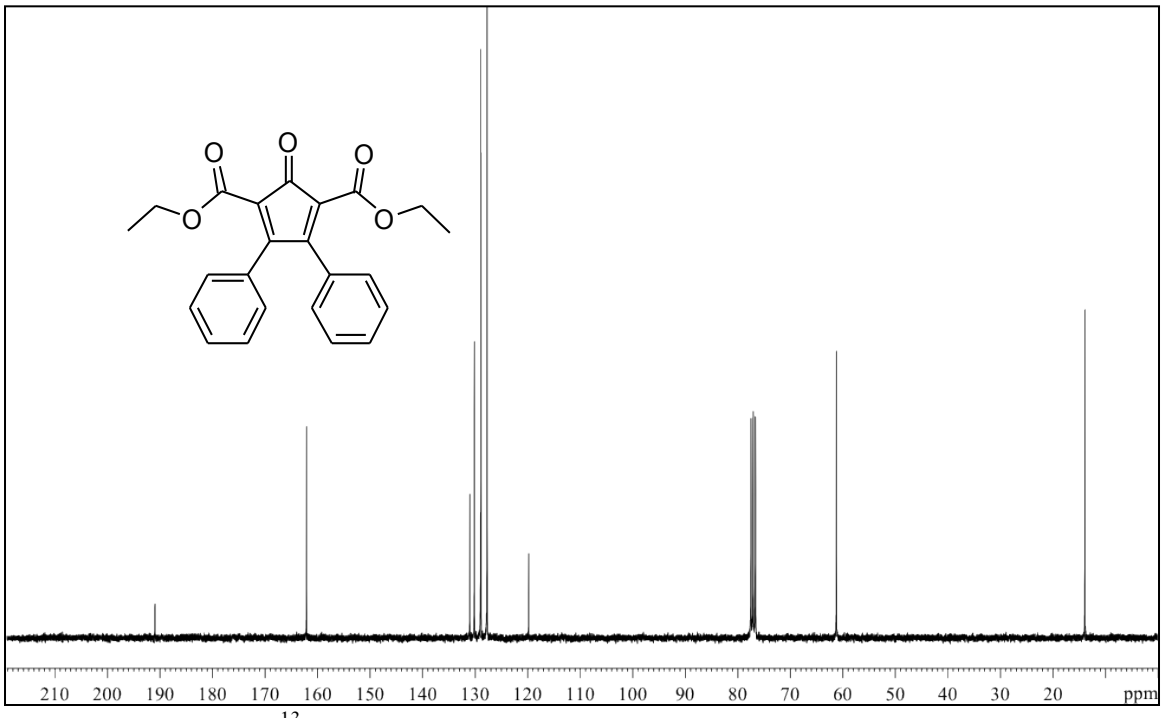


Figure 34: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **91**.

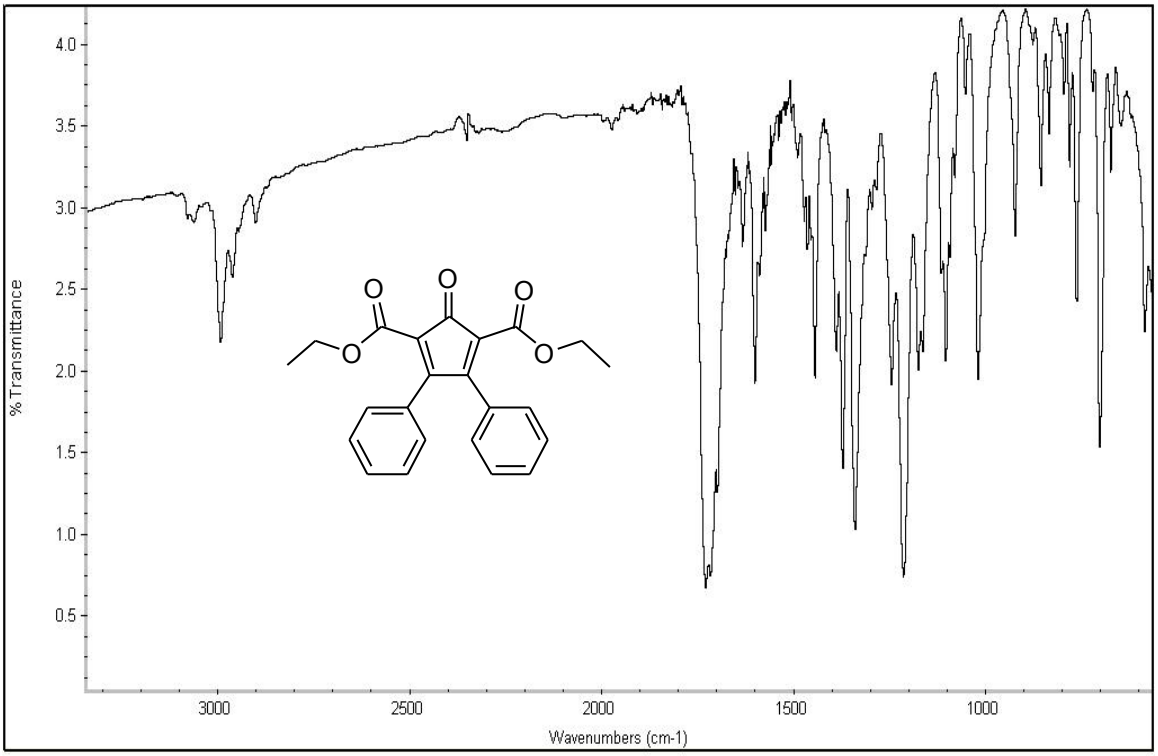


Figure 35: IR Spectrum (NaCl) of **91**.

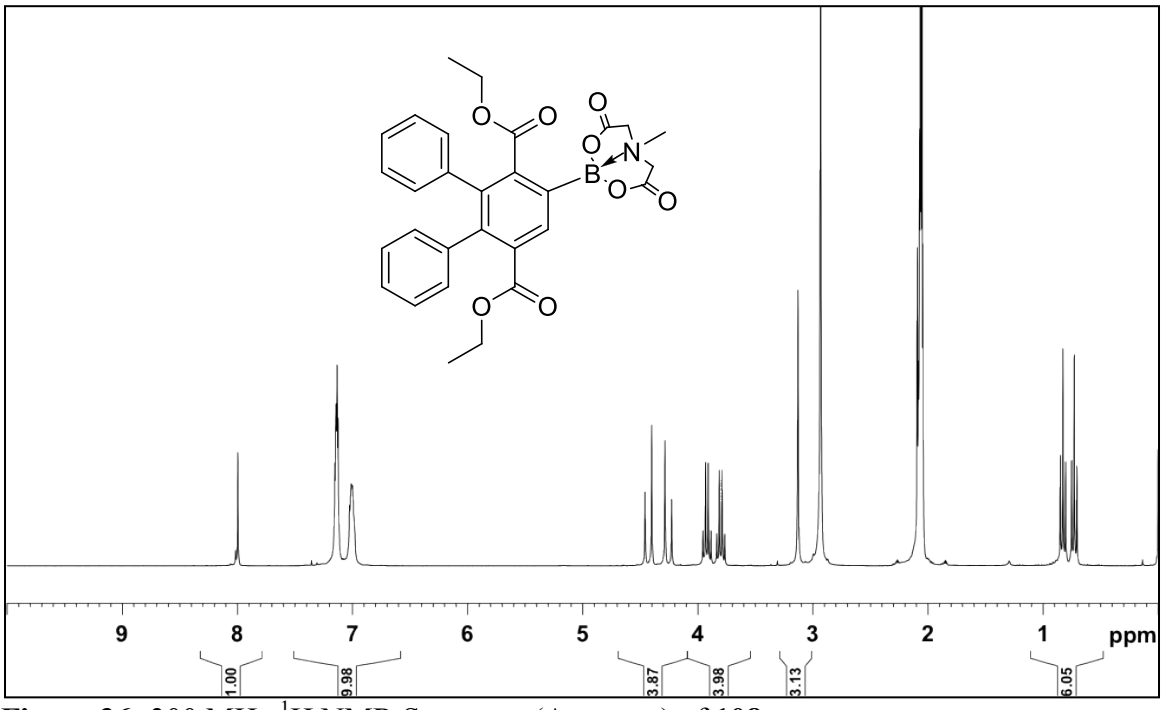


Figure 36: 300 MHz ^{1}H NMR Spectrum (Acetone$_6$) of **108**.

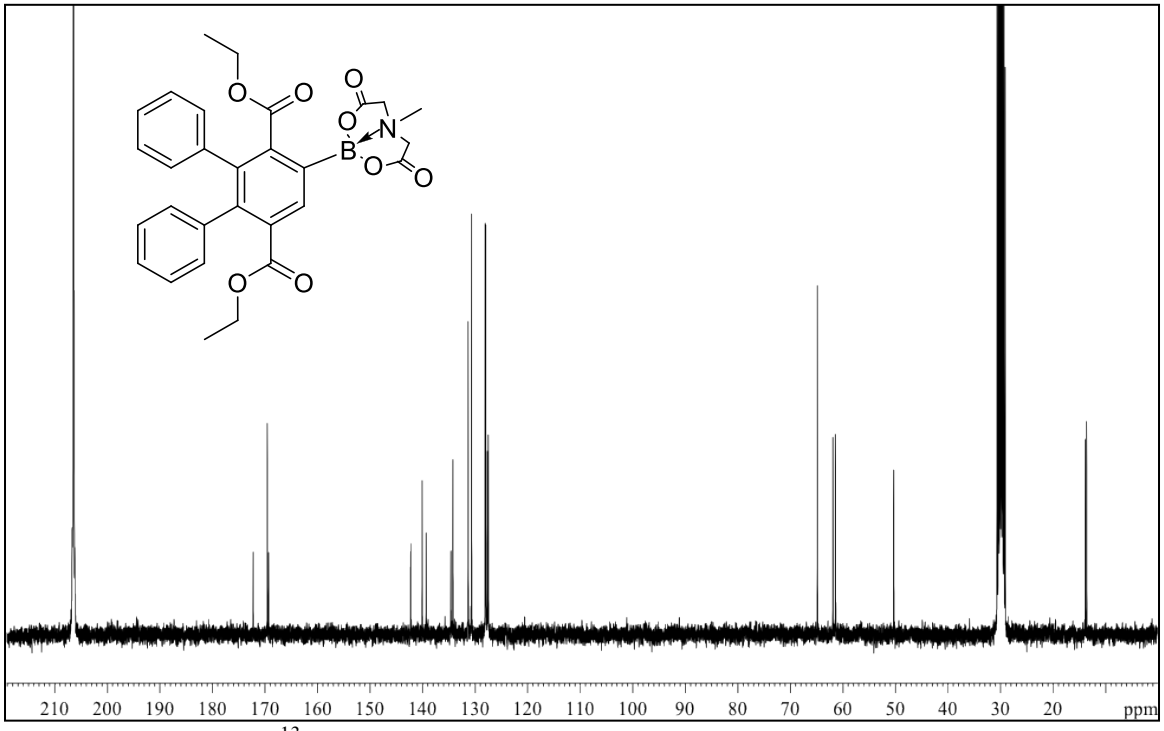


Figure 37: 300 MHz ^{13}C NMR Spectrum (Acetone$_6$) of **108**.

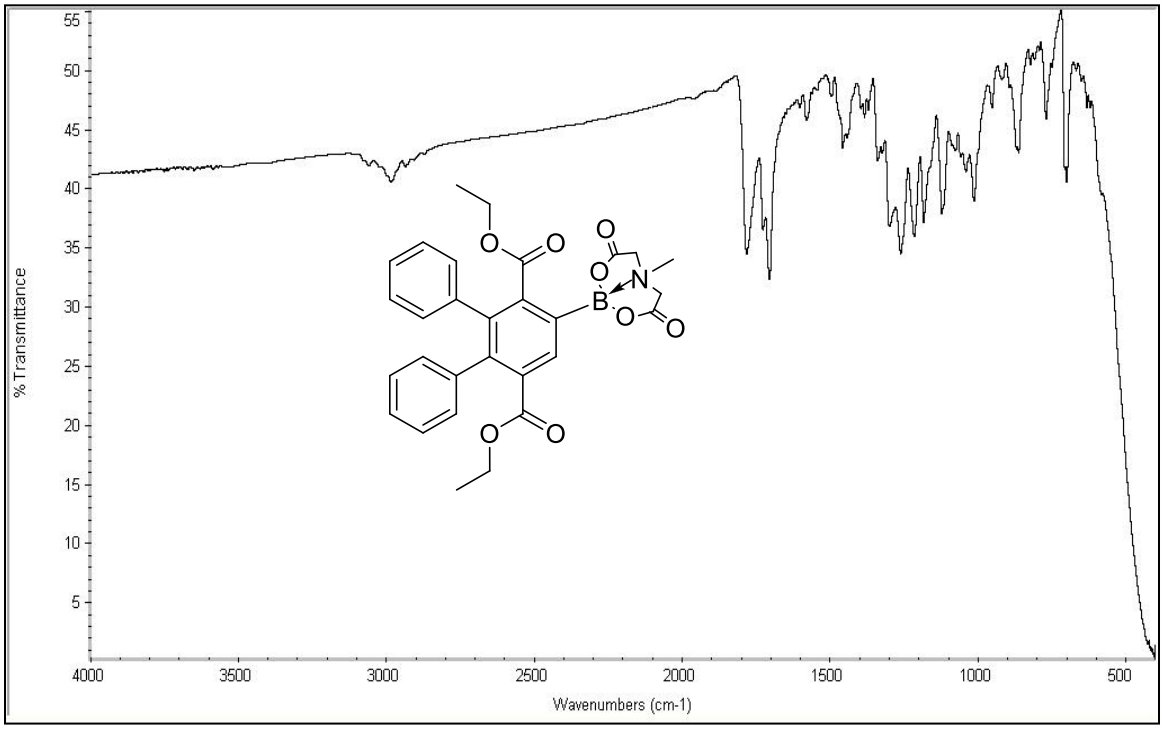


Figure 38: IR Spectrum (NaCl) of **108**.

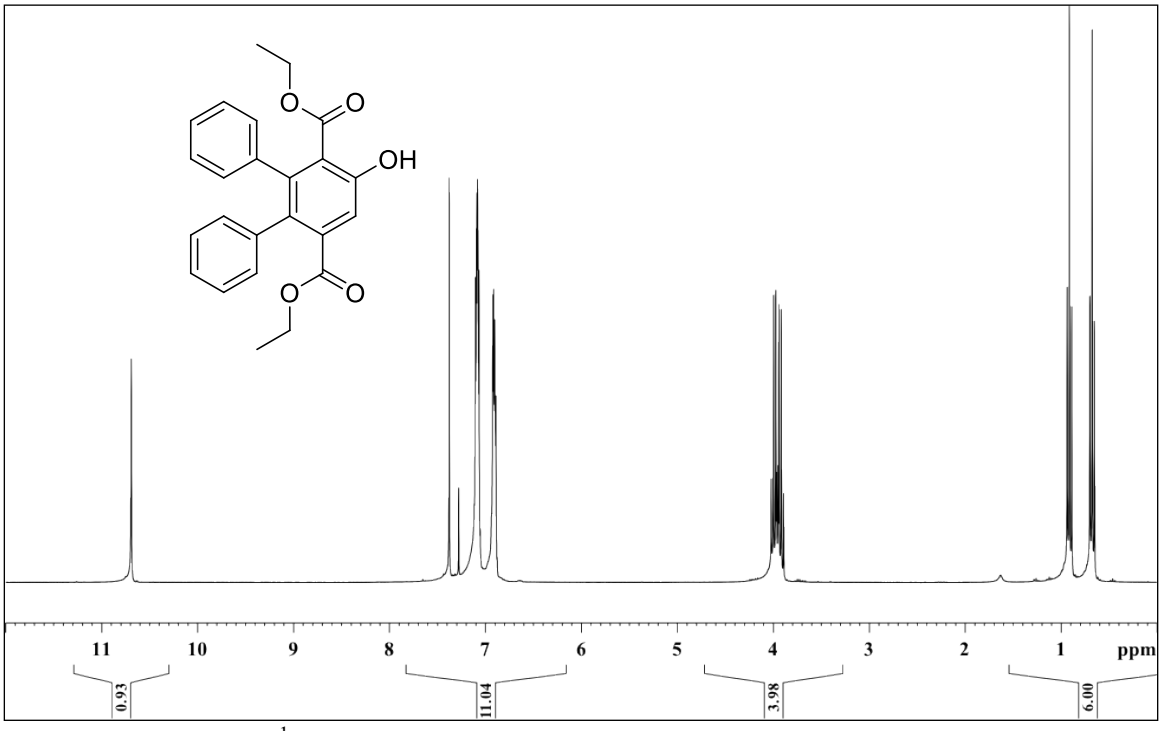


Figure 39: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **94**.

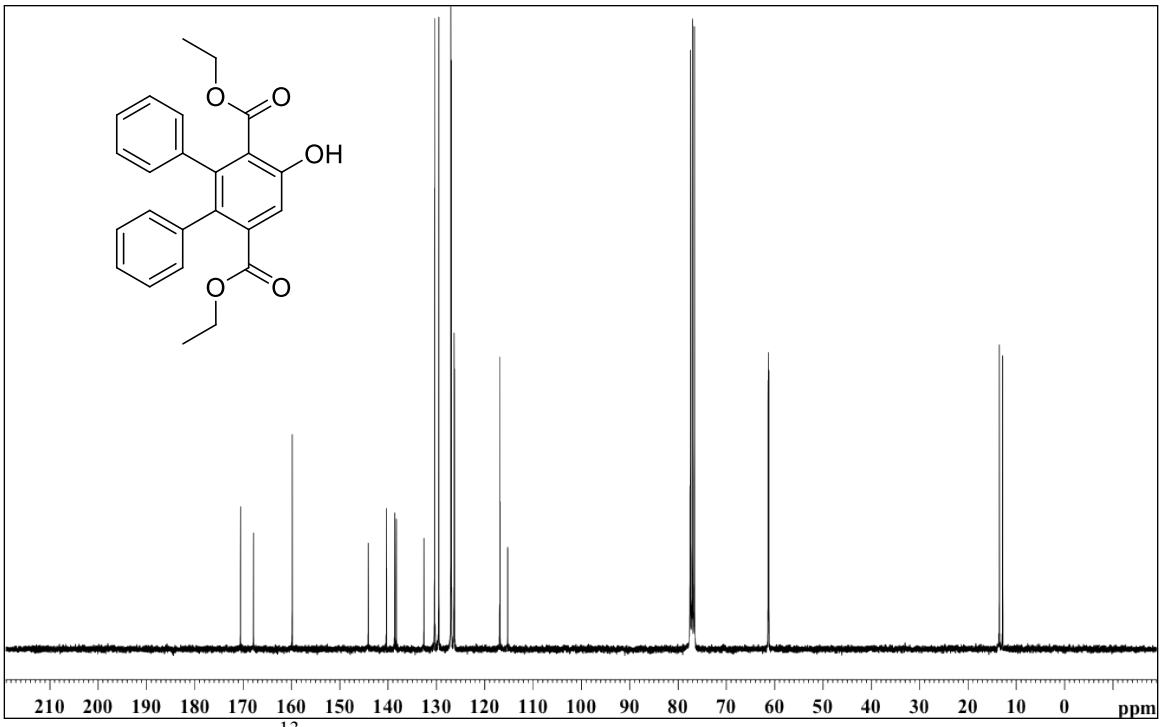


Figure 40: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **94**.

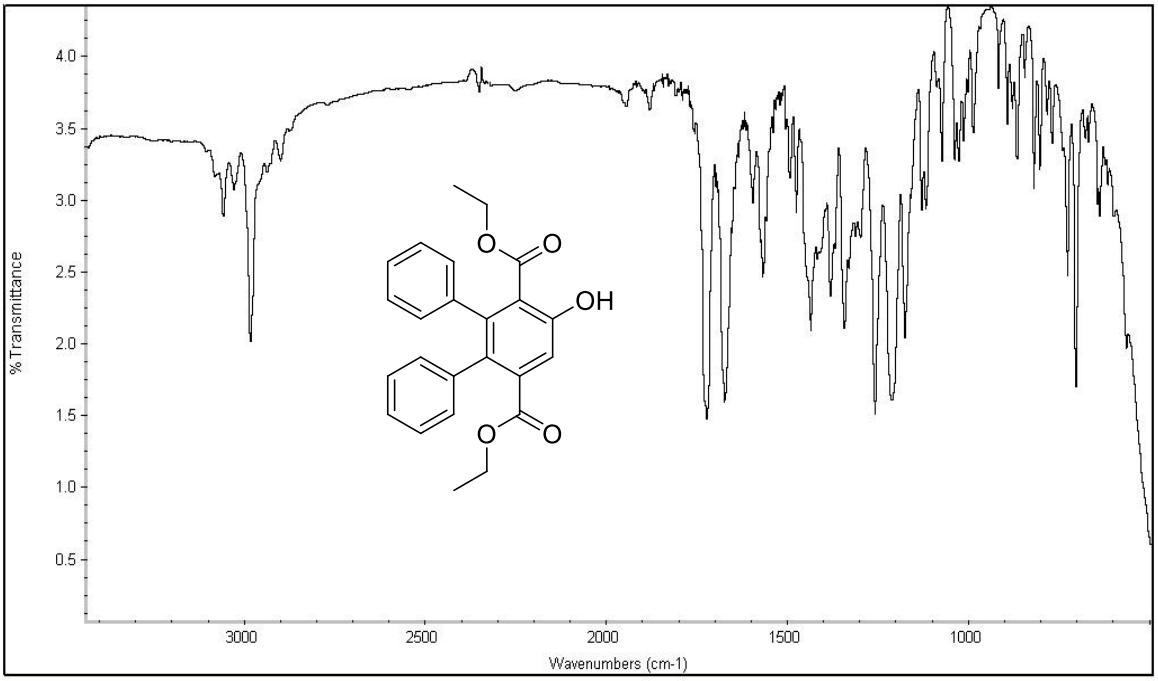


Figure 41: IR Spectrum (NaCl) of **94**.

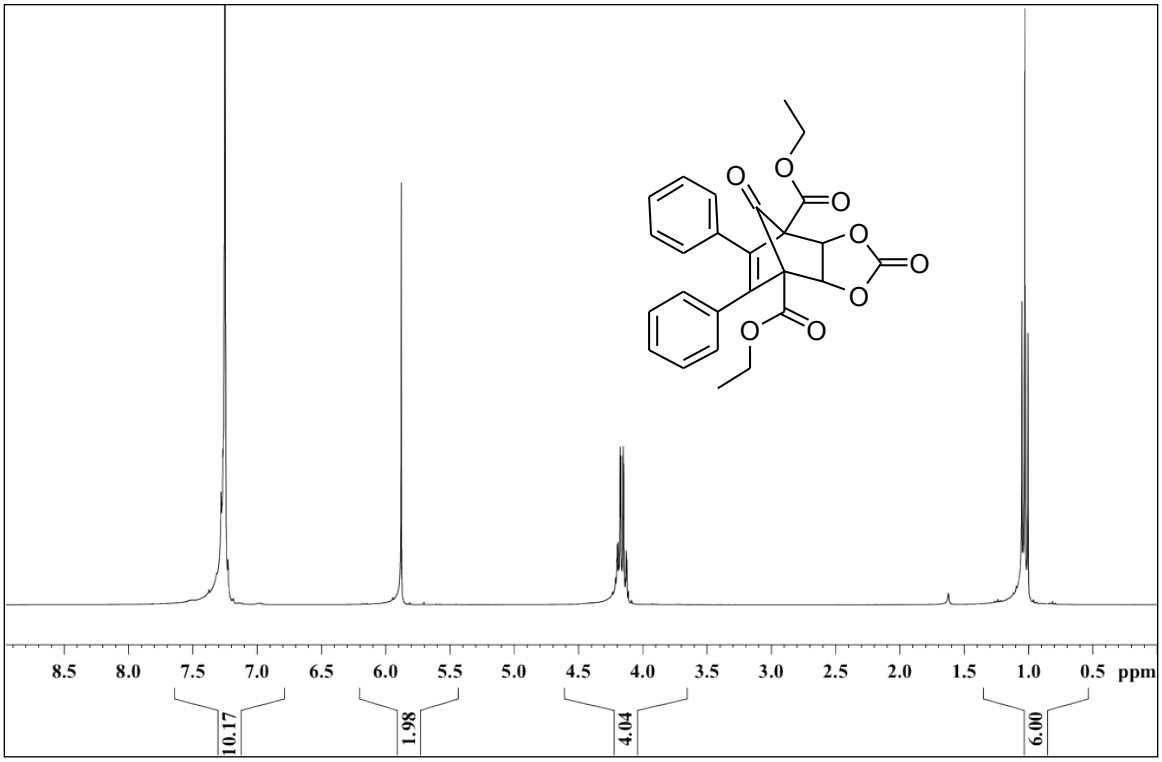


Figure 42: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **92**.

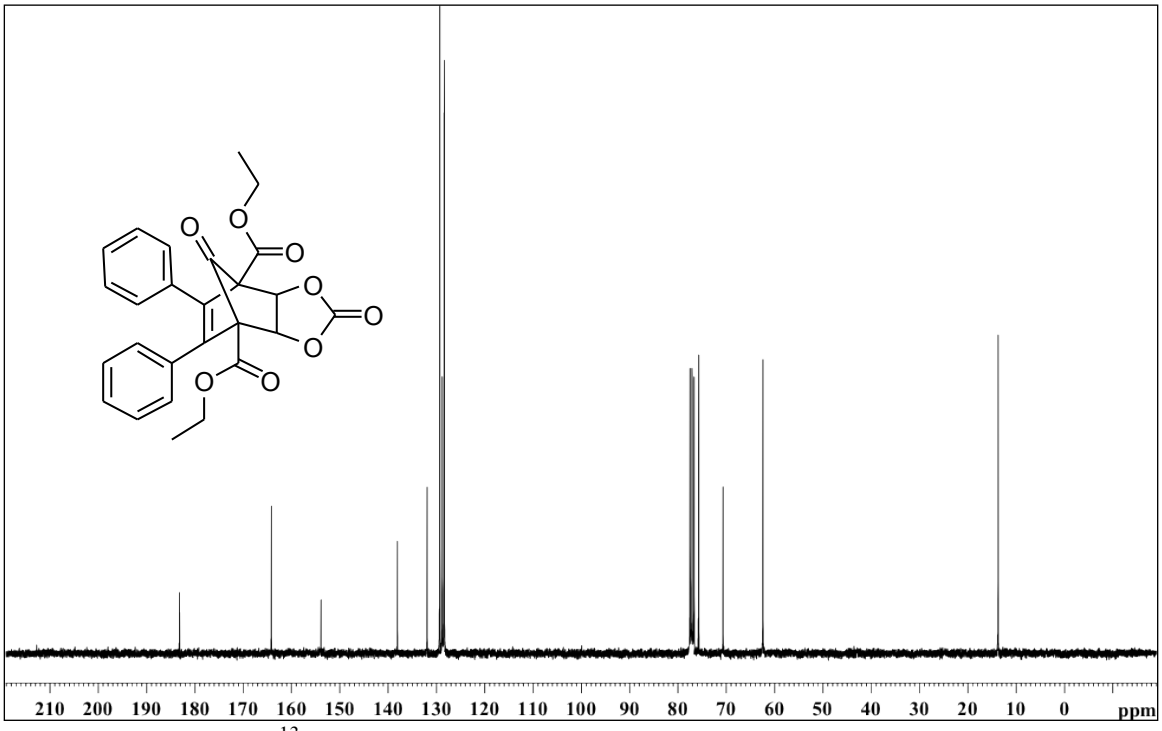


Figure 43: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **92**.

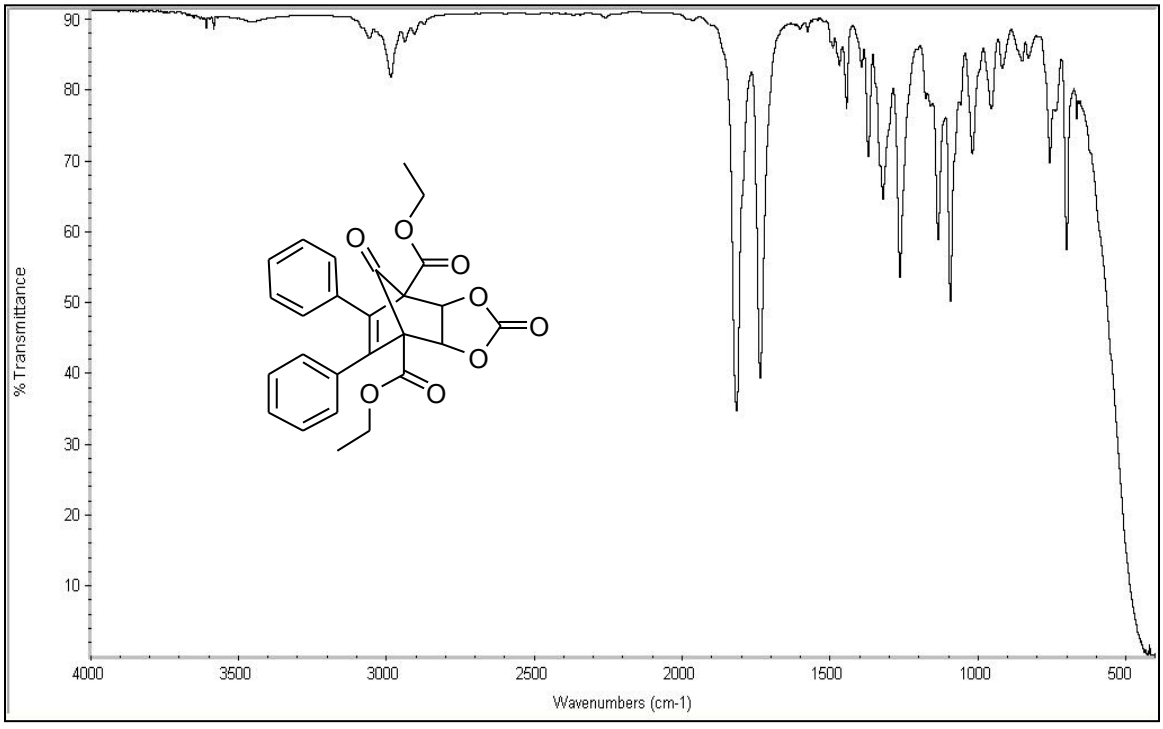


Figure 44: IR Spectrum (NaCl) of **92**.

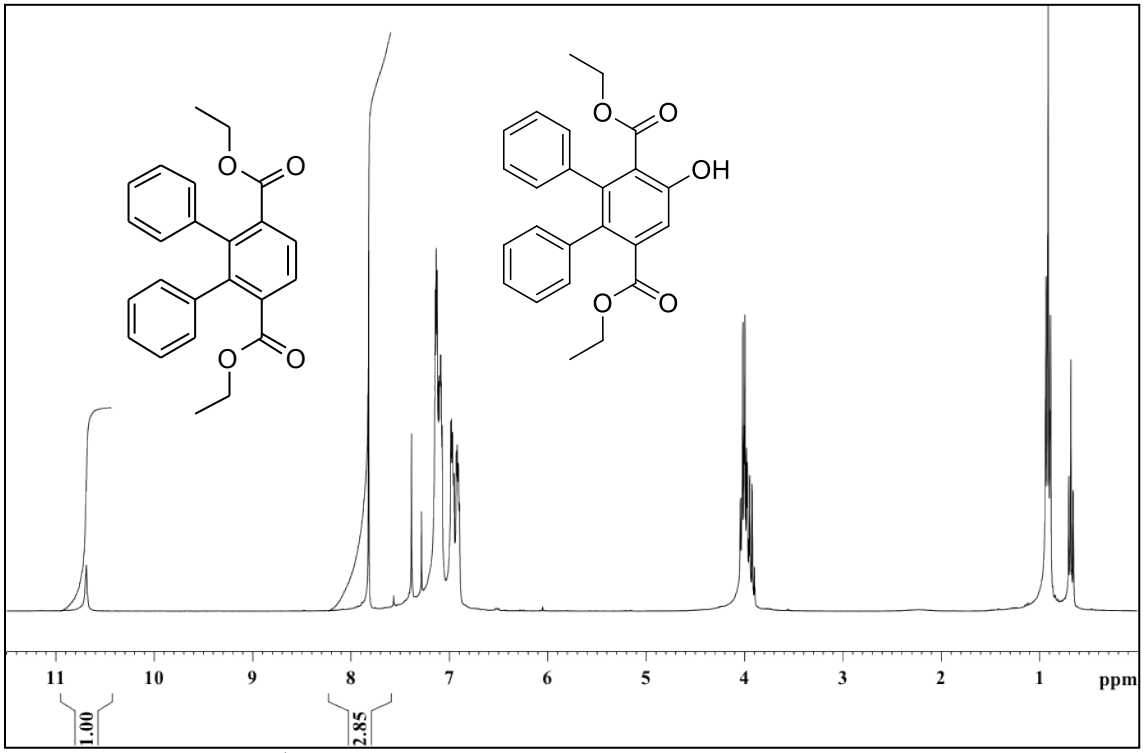


Figure 45: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **94** and **109**.

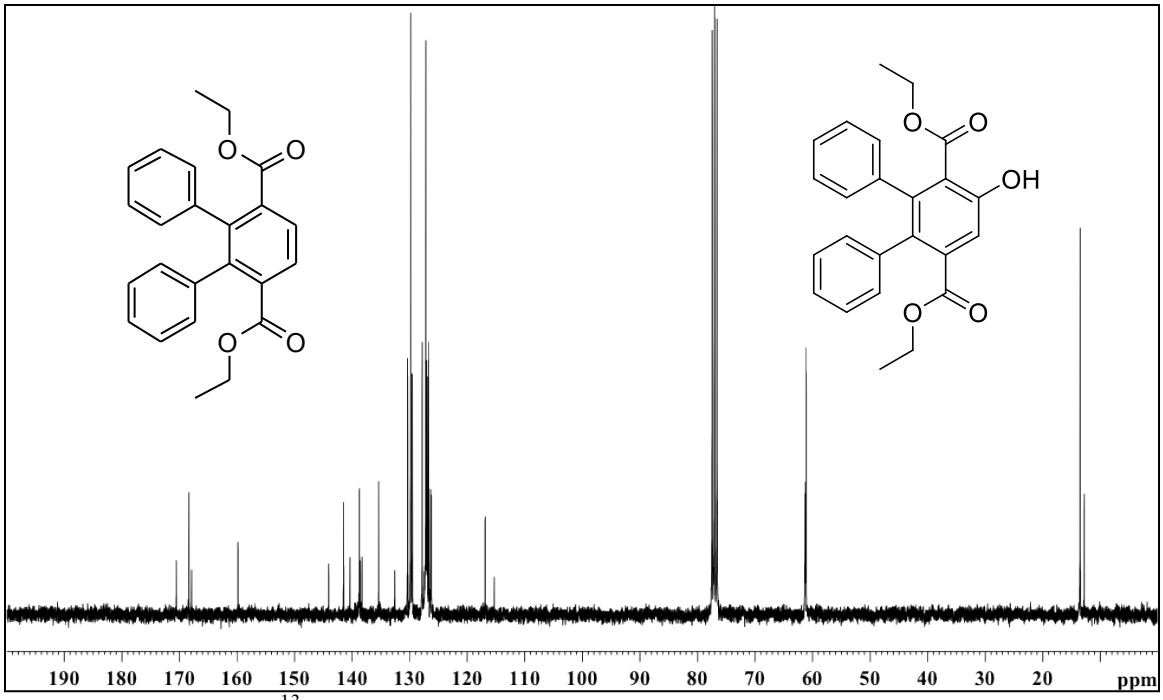


Figure 46: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **94** and **109**.

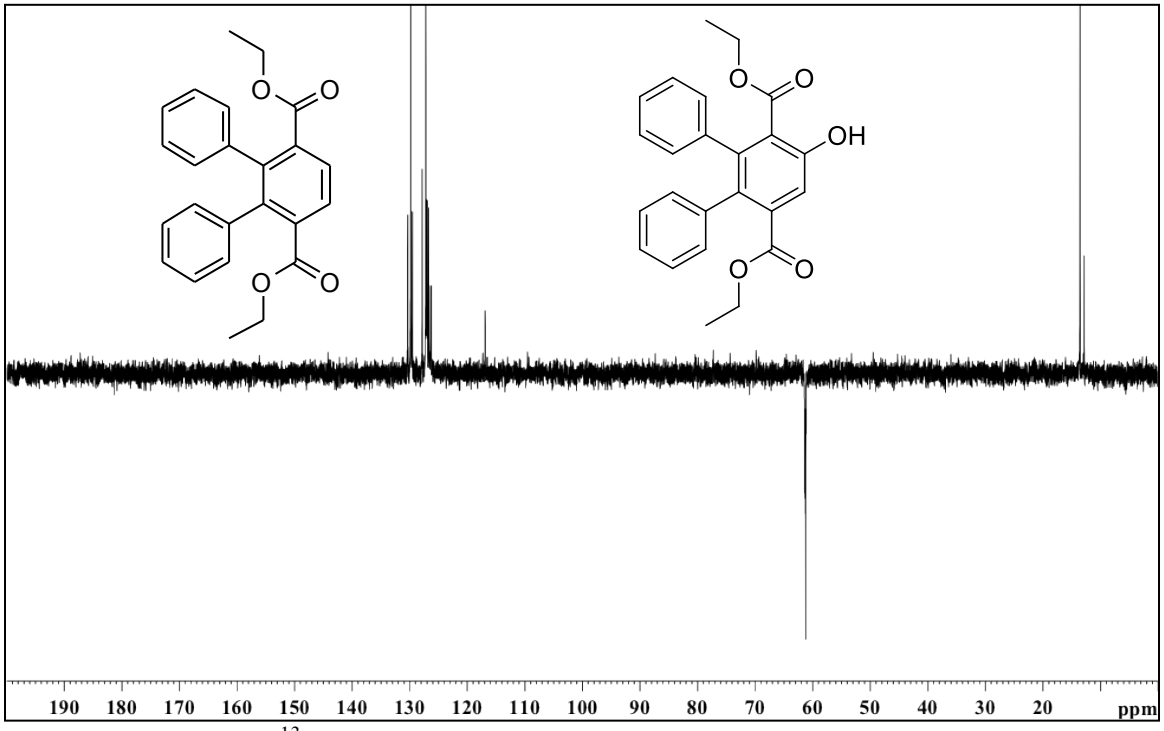


Figure 47: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) DEPT 135 of **94** and **109**.

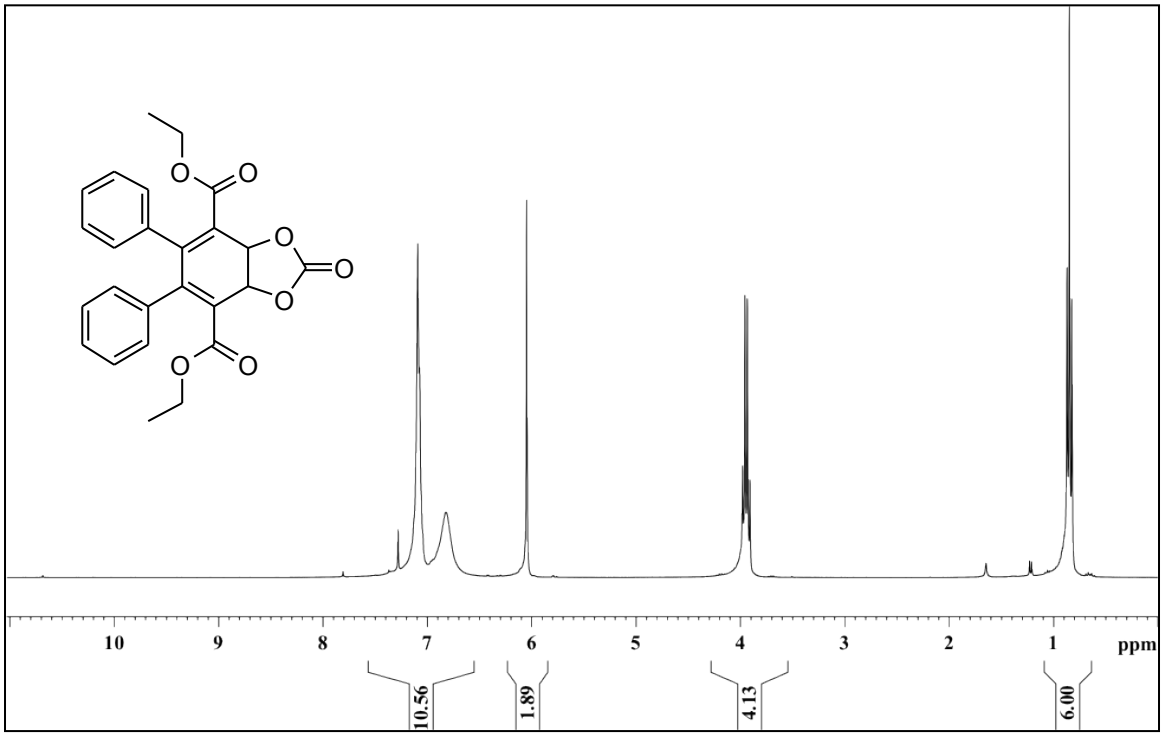


Figure 48: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **93**.

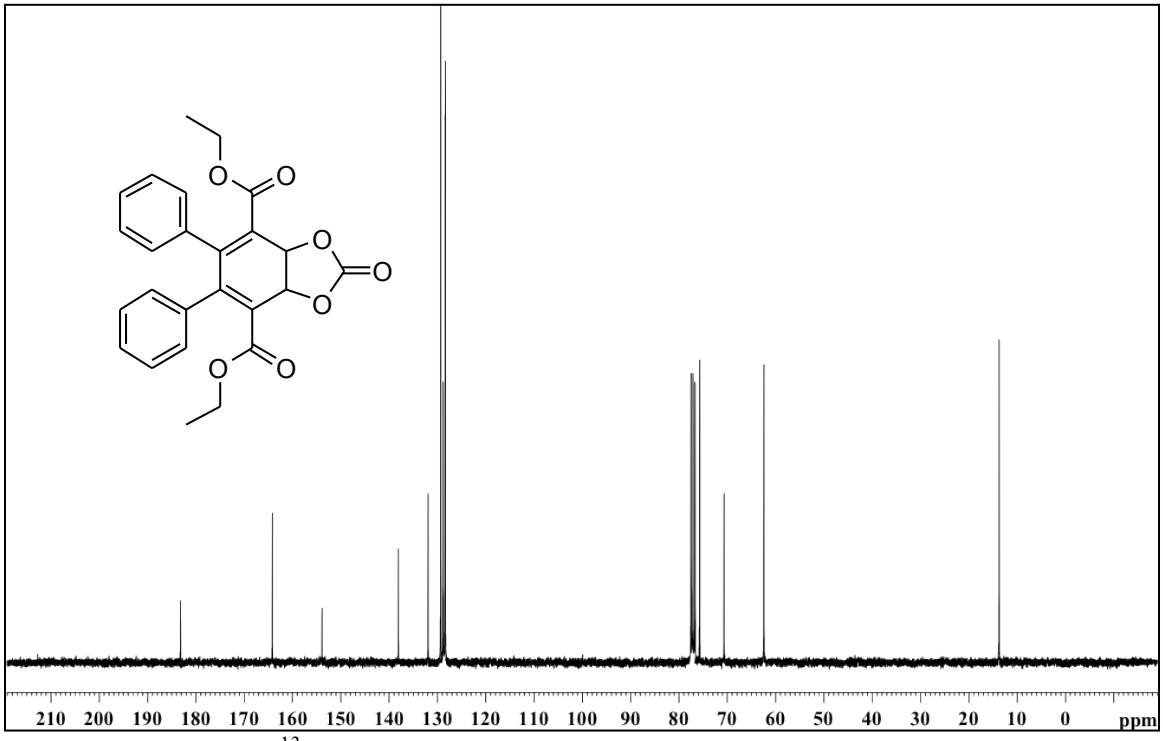


Figure 49: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **93**.

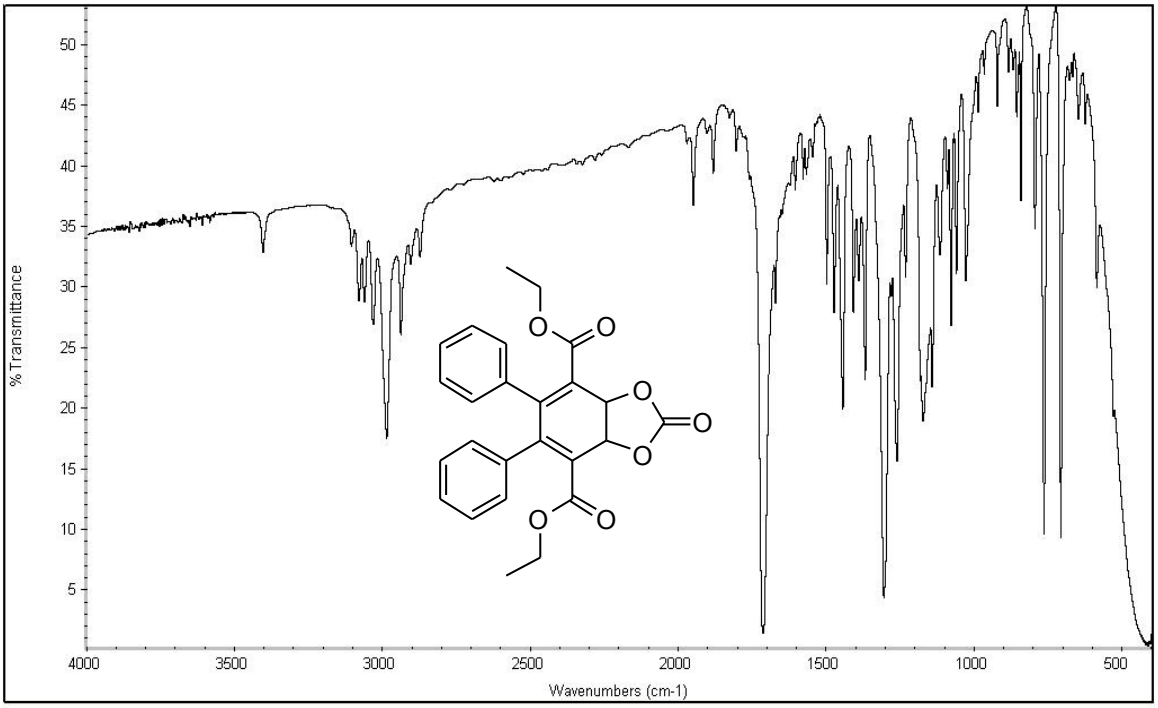


Figure 50: IR Spectrum (NaCl) of **93**.

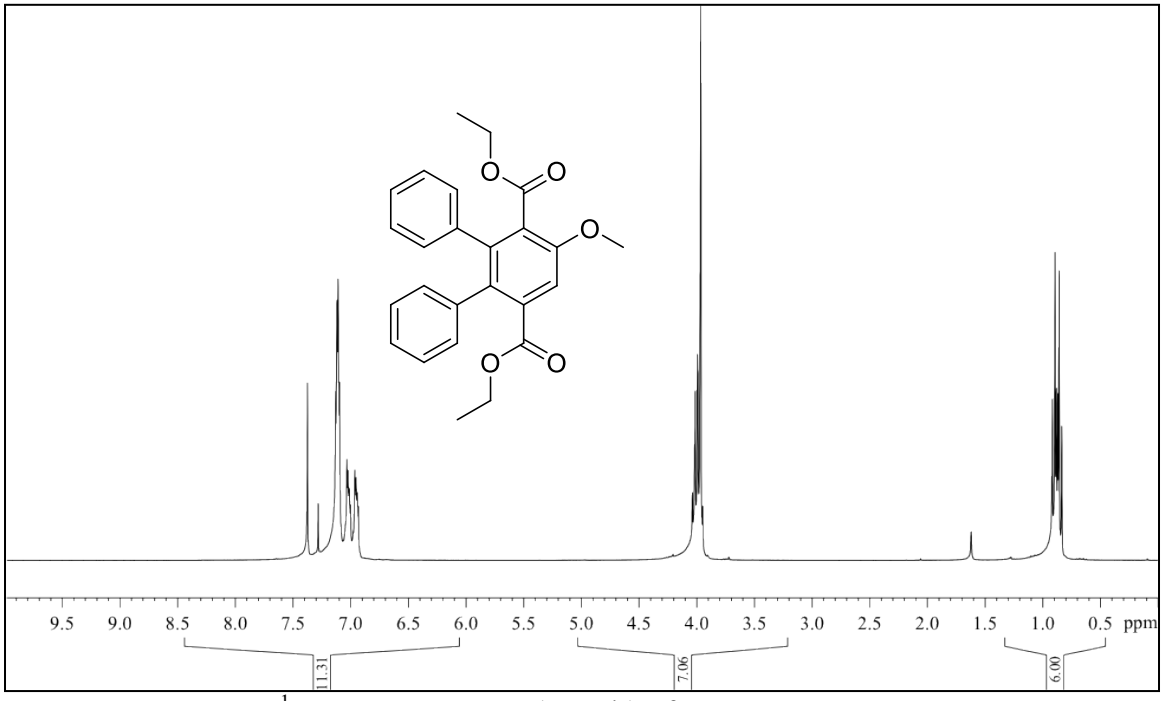


Figure 51: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **111a**.

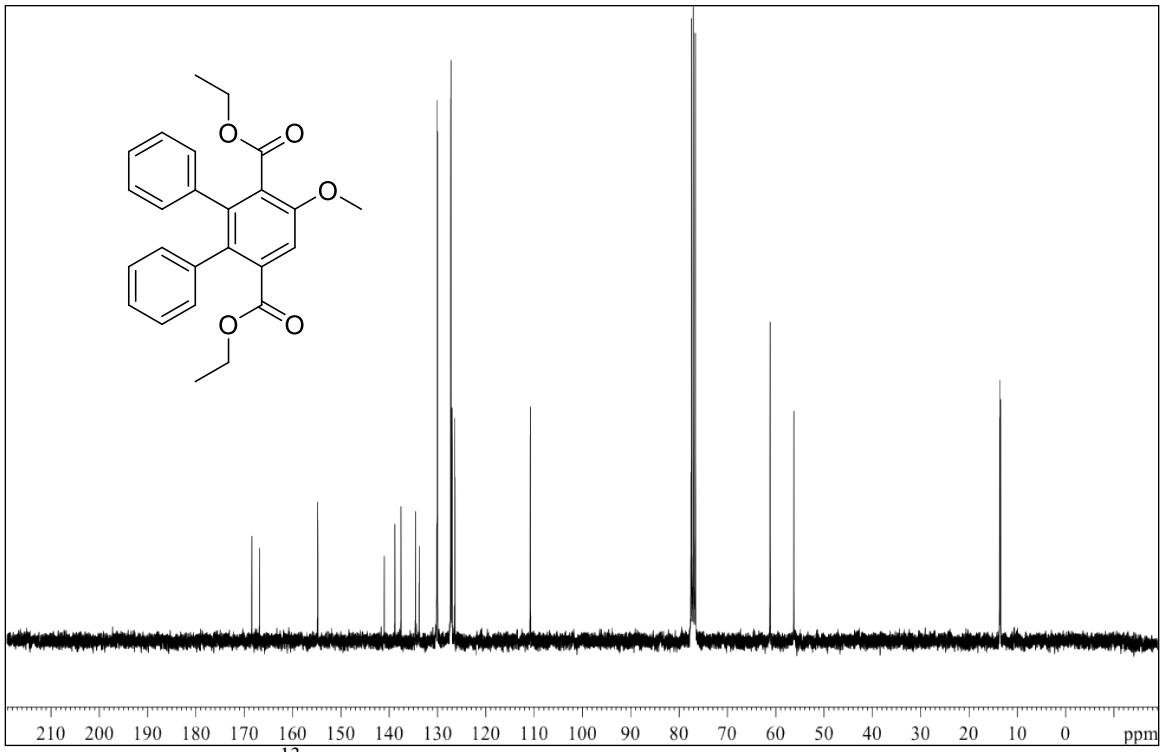


Figure 52: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **111a**.

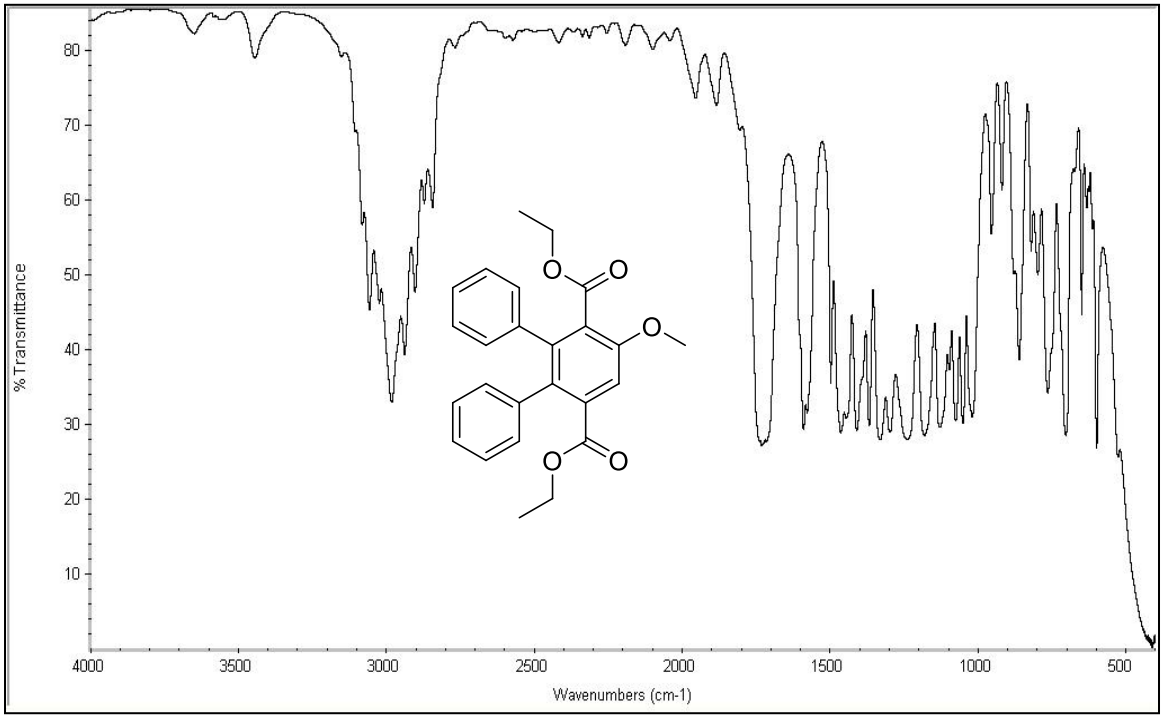


Figure 53: IR Spectrum (NaCl) of **111a**.

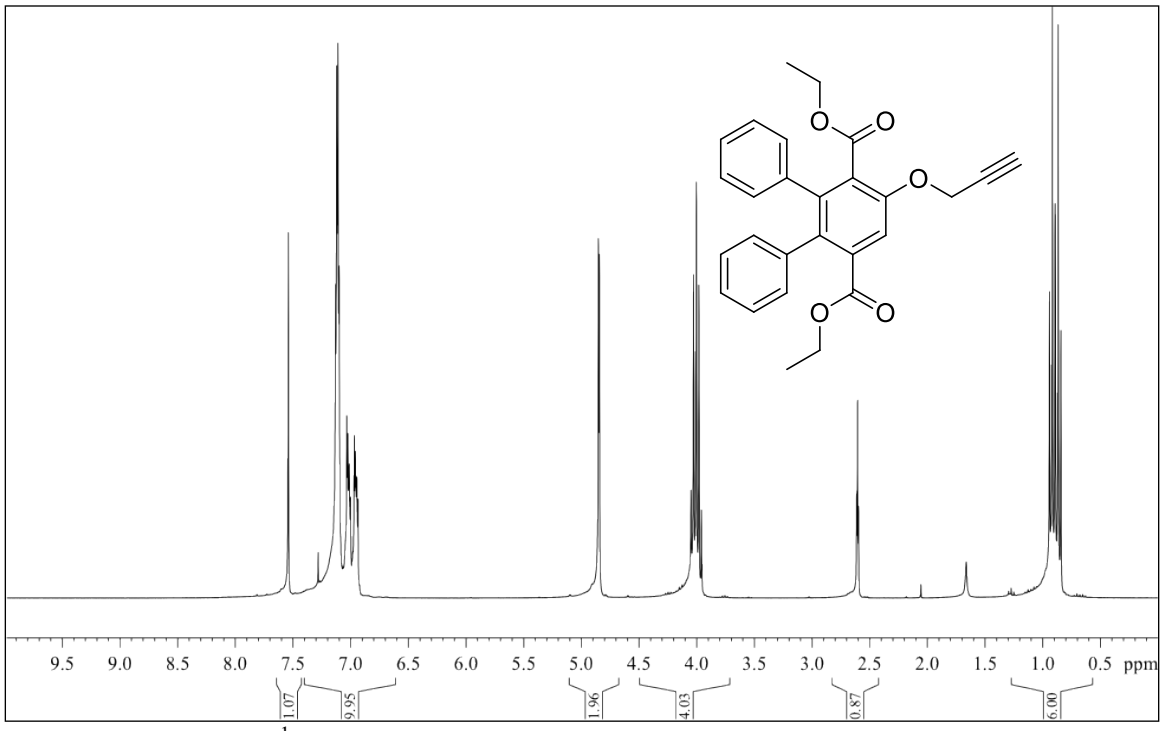


Figure 54: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **111b**.

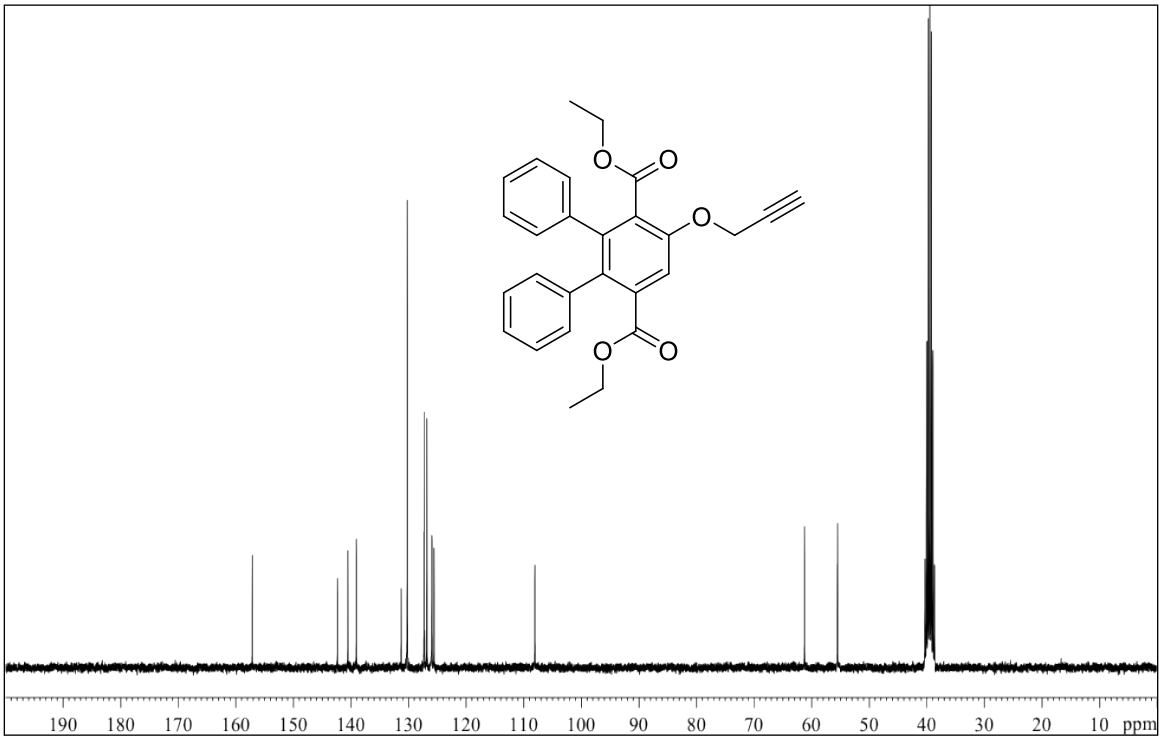


Figure 55: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **111b**.

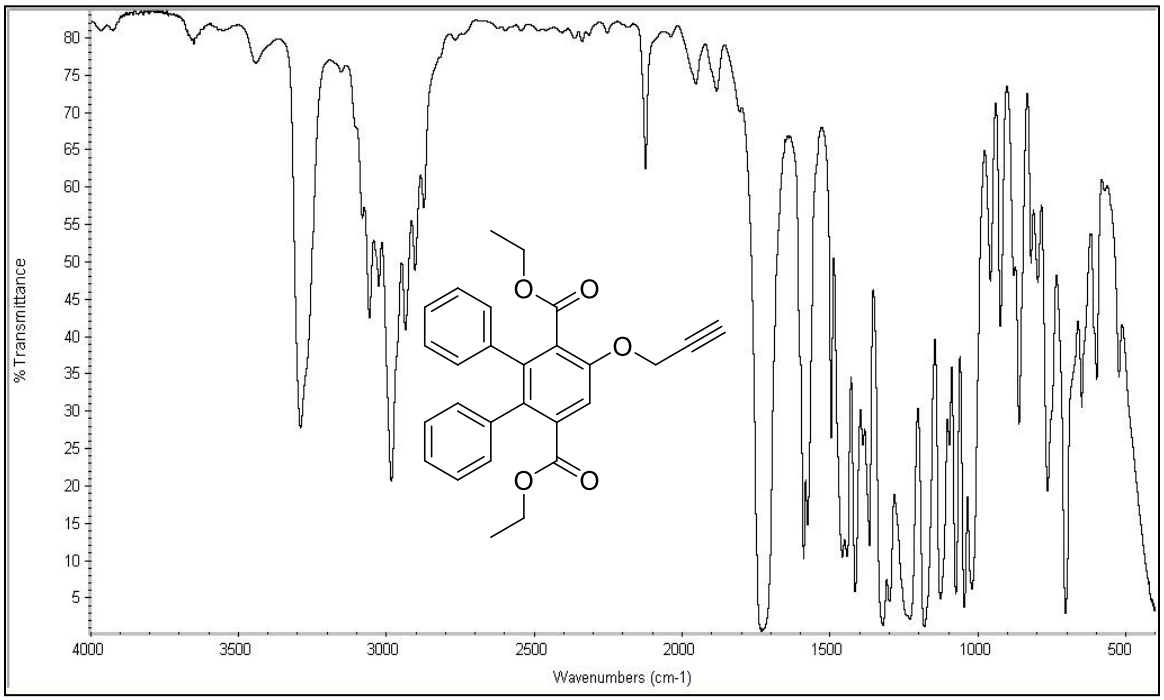


Figure 56: IR Spectrum (NaCl) of **111b**.

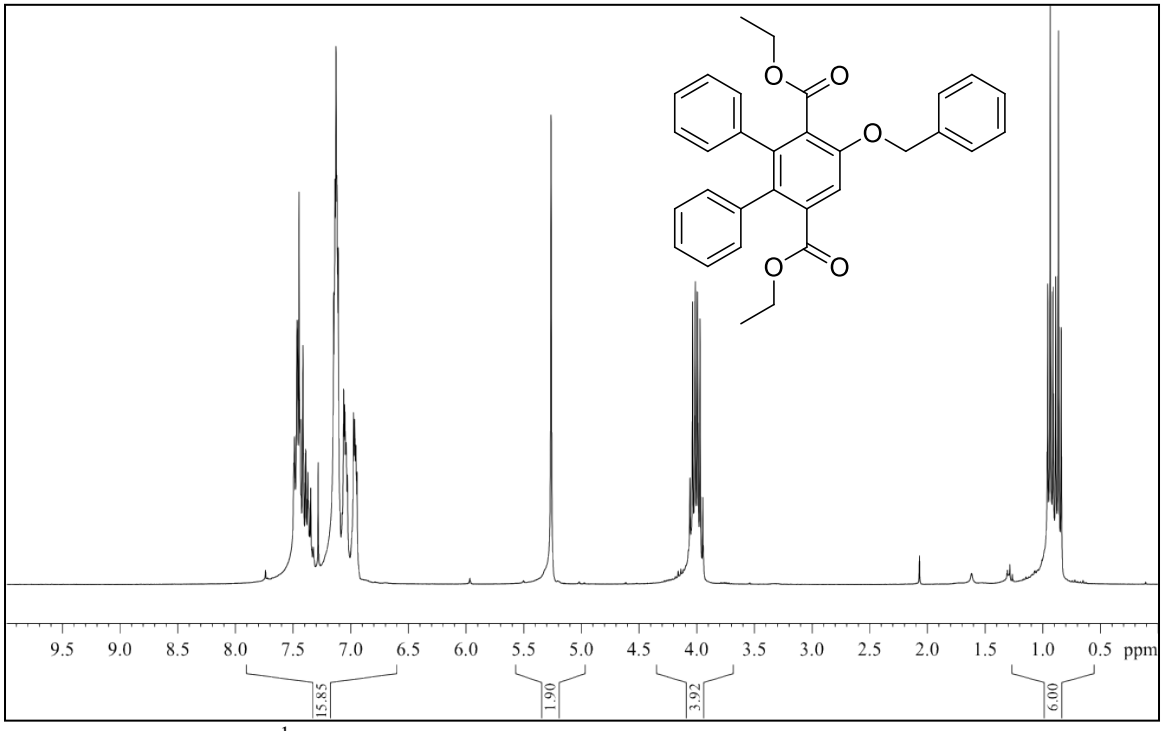


Figure 57: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **111c**.

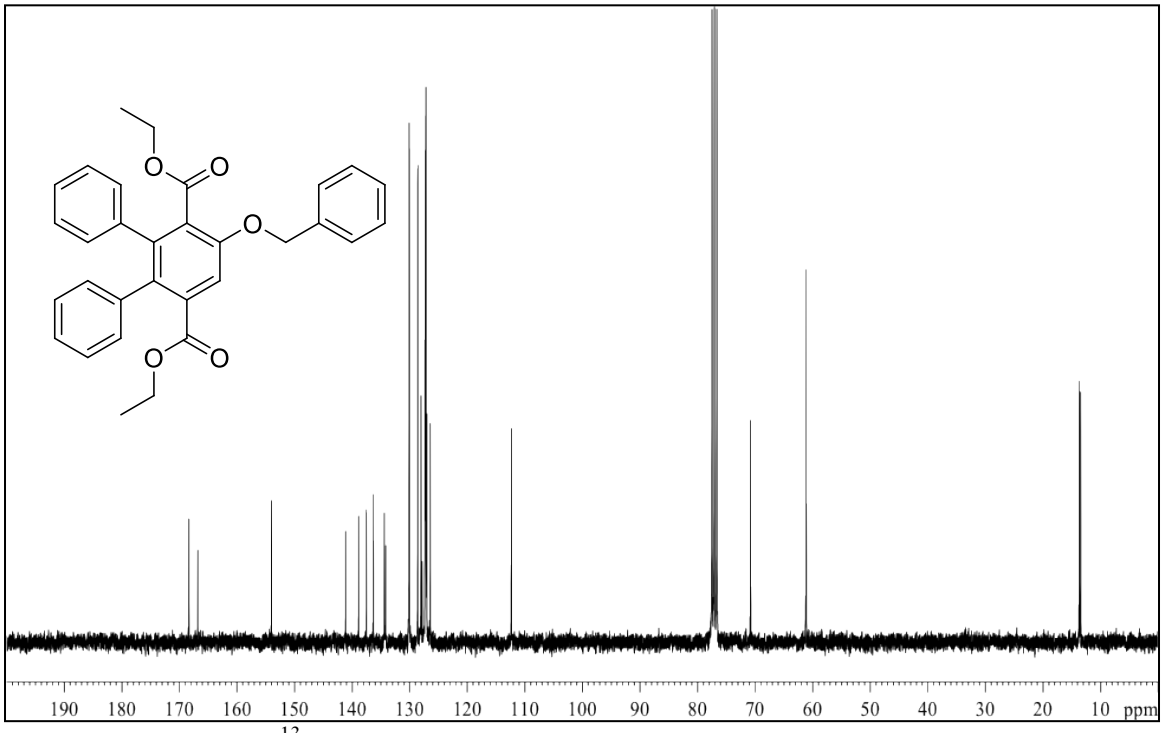


Figure 58: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **111c**.

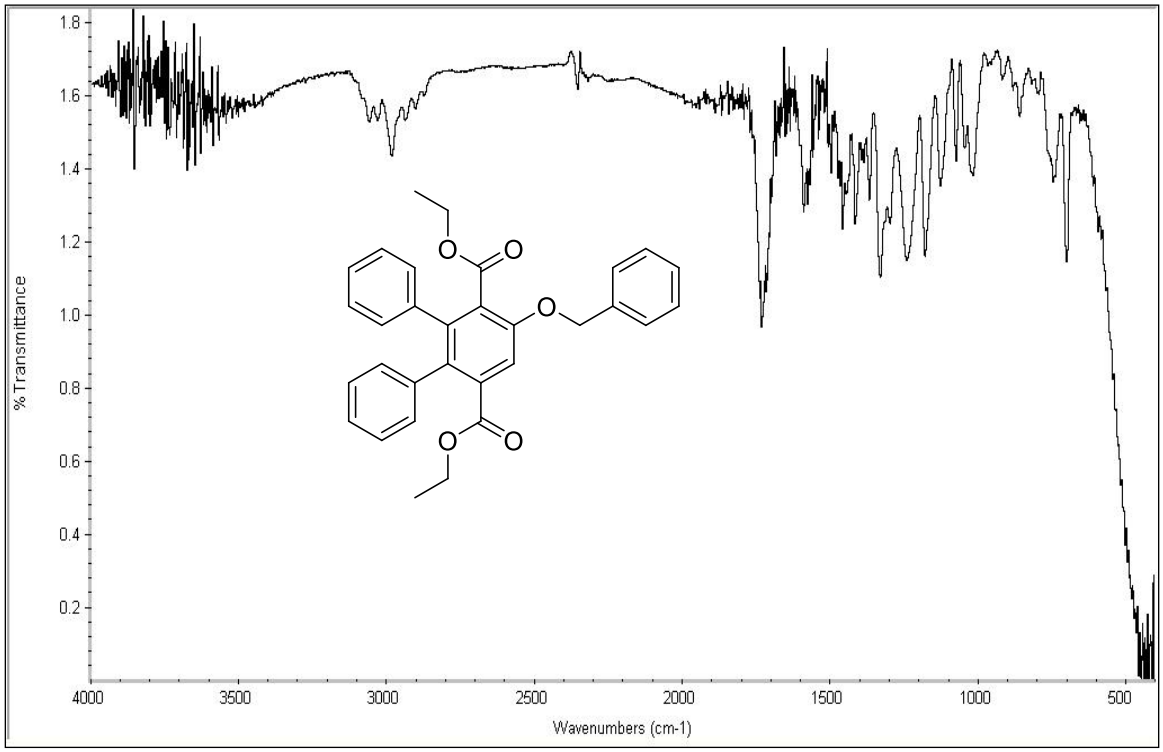


Figure 59: IR Spectrum (NaCl) of **111c**.

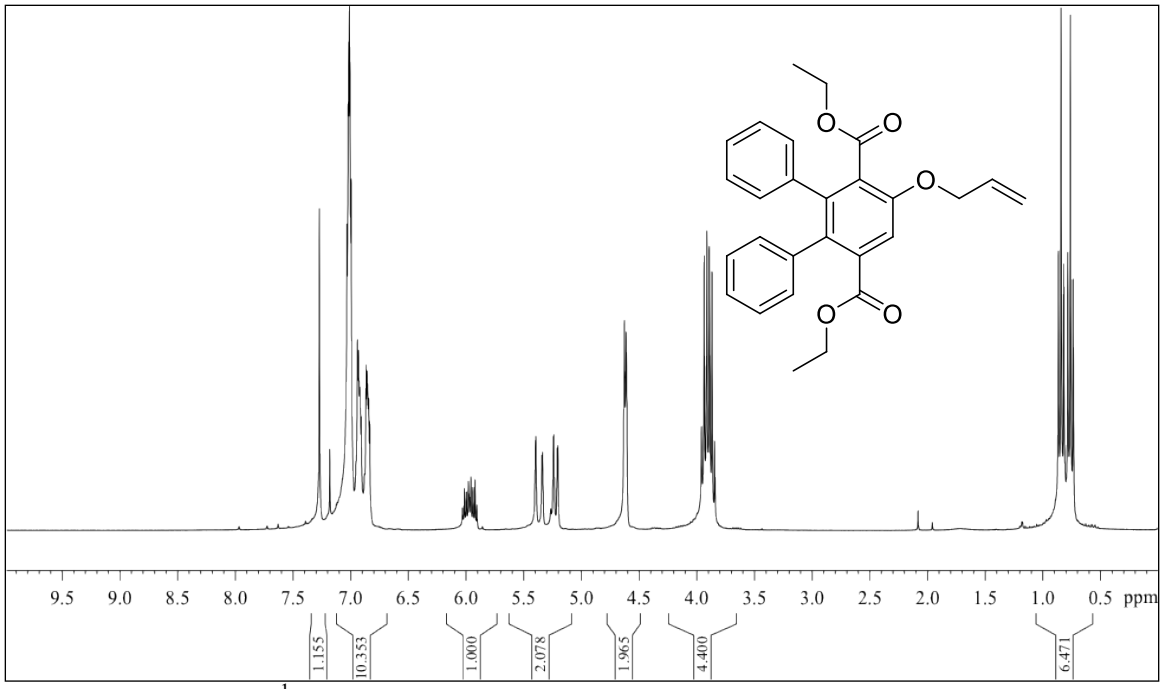


Figure 60: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **111d**.

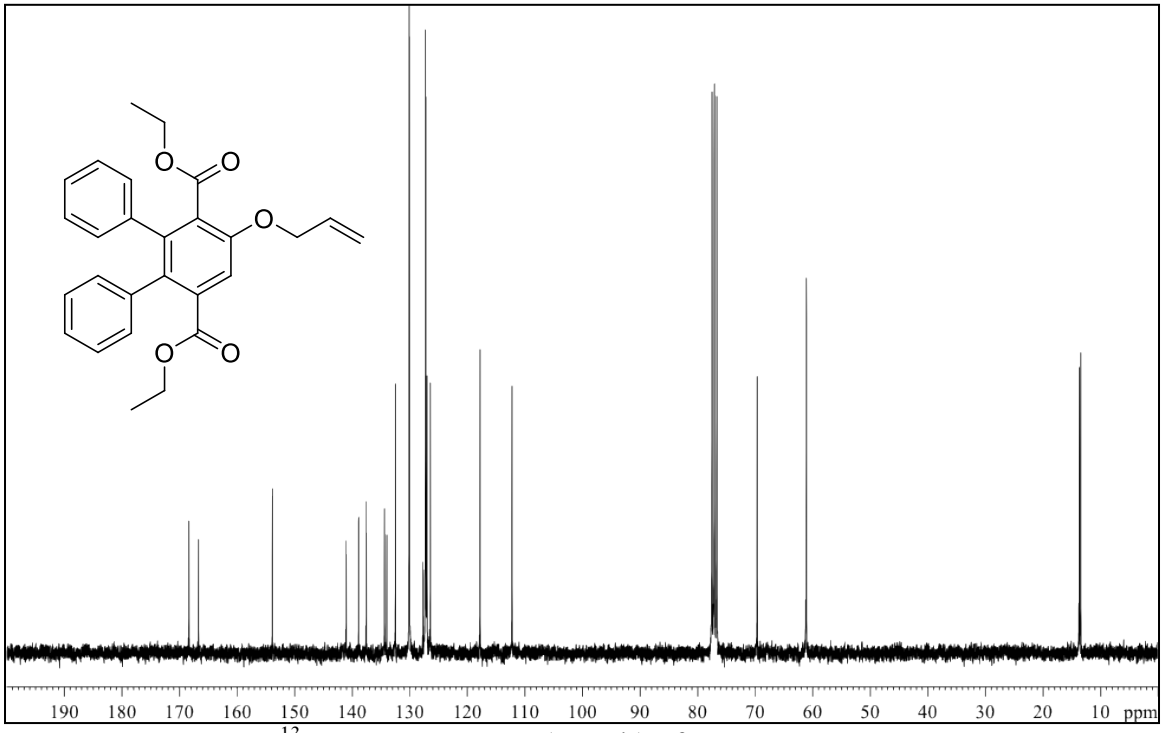


Figure 61: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **111d**.

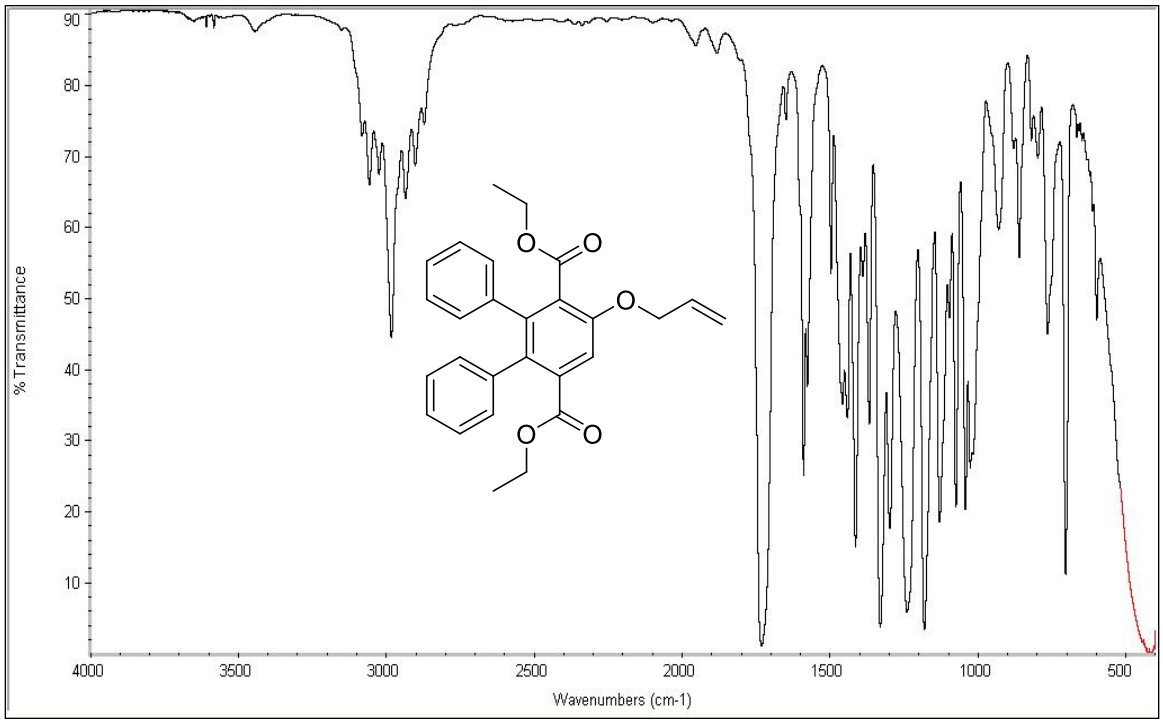


Figure 62: IR Spectrum (NaCl) of **111d**.

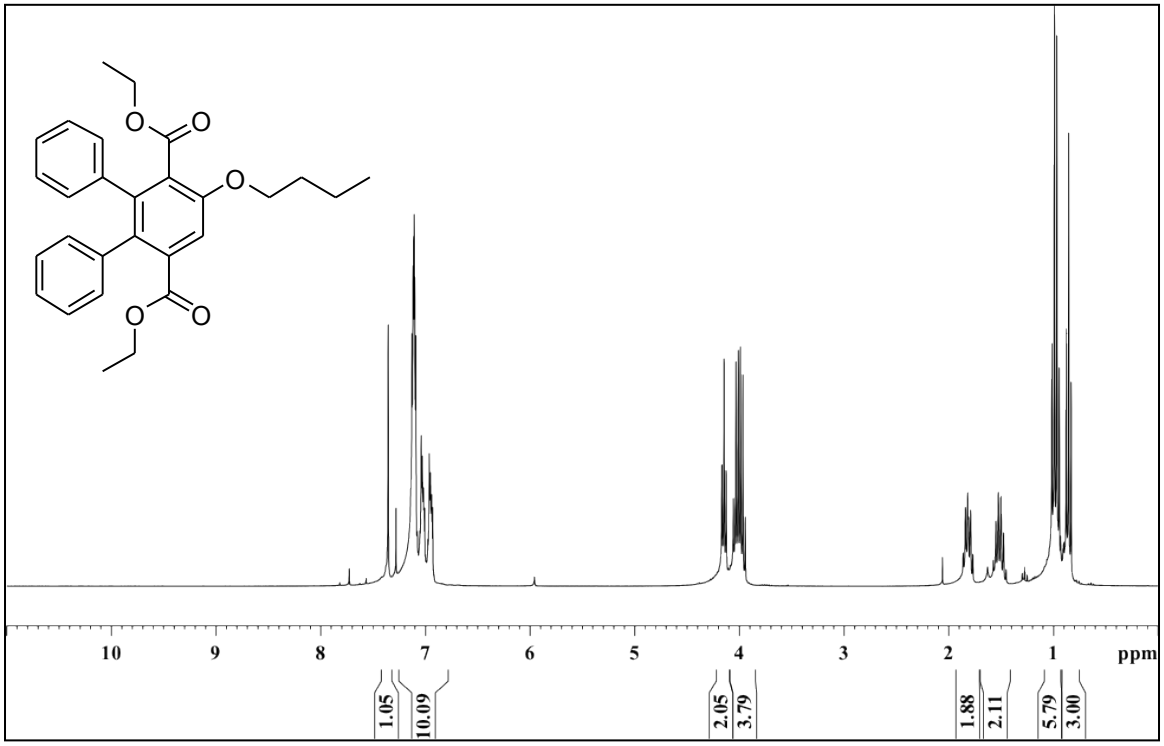


Figure 63: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **111e**.

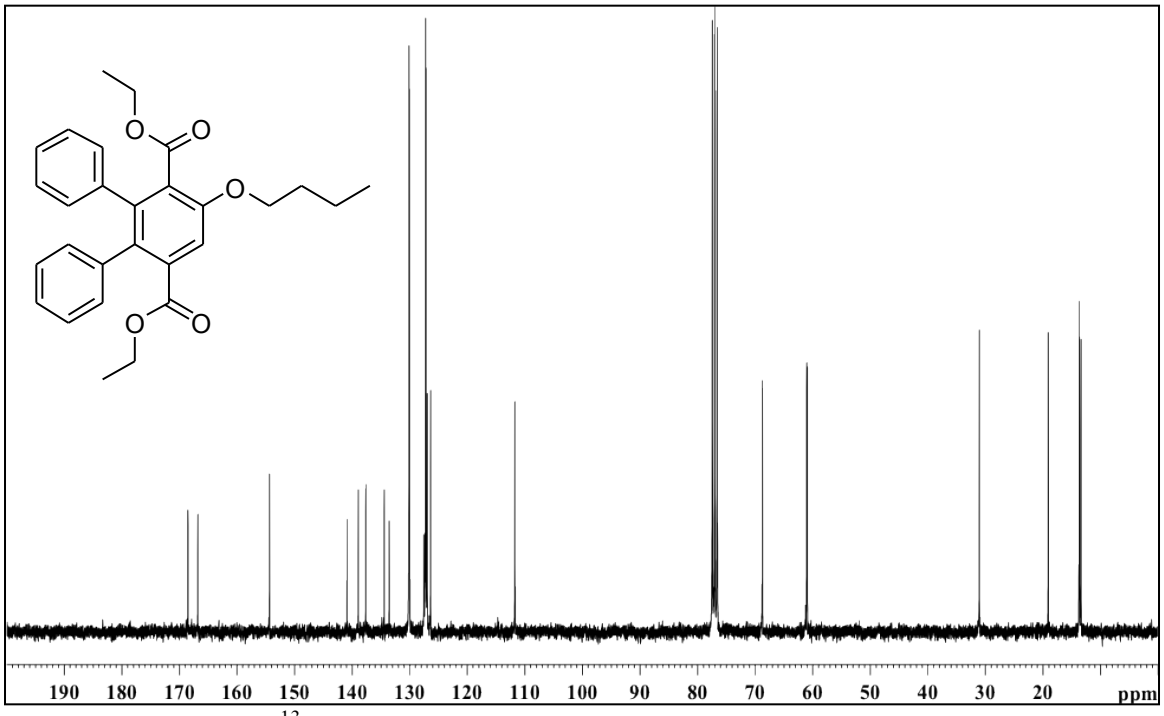


Figure 64: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **111e**.

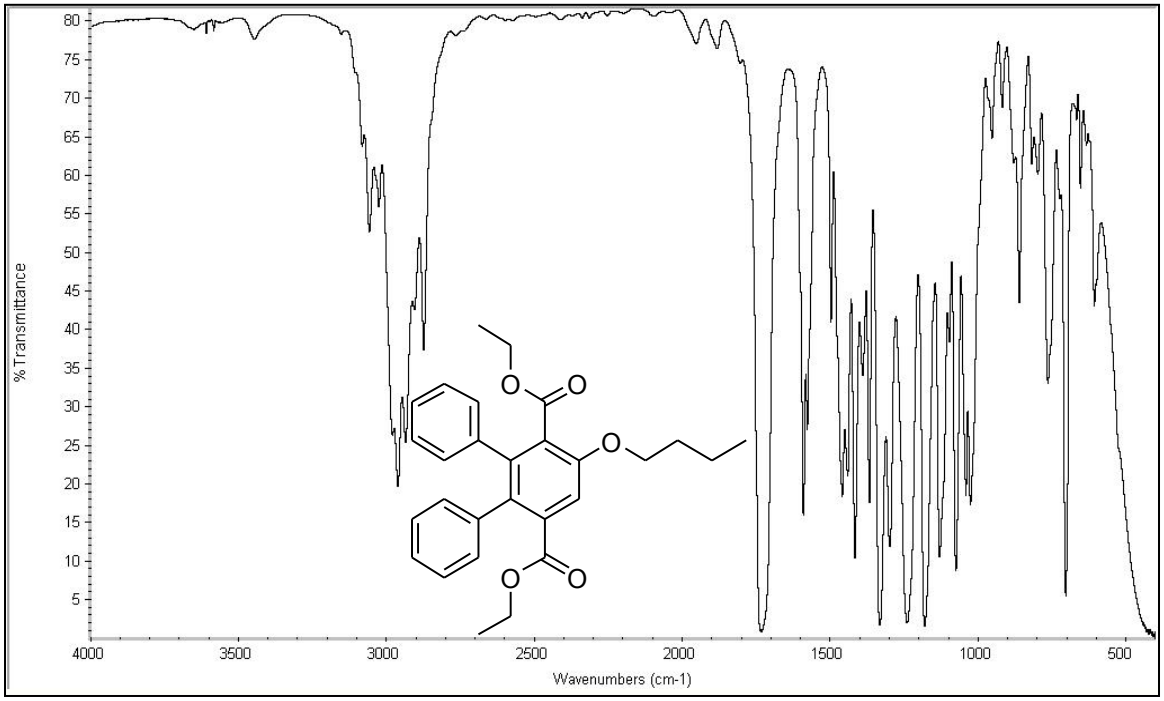


Figure 65: IR Spectrum (NaCl) of **111e**.

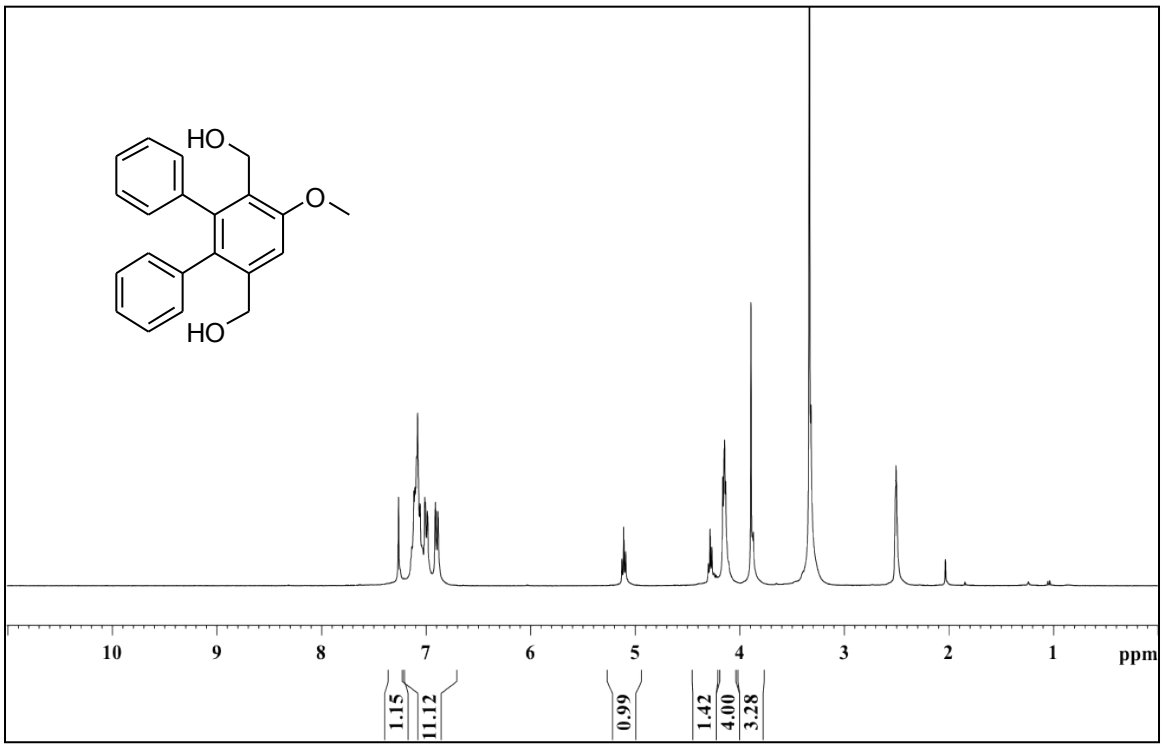


Figure 66: 300 MHz ^{1}H NMR Spectrum (DMSO) of **112a**.

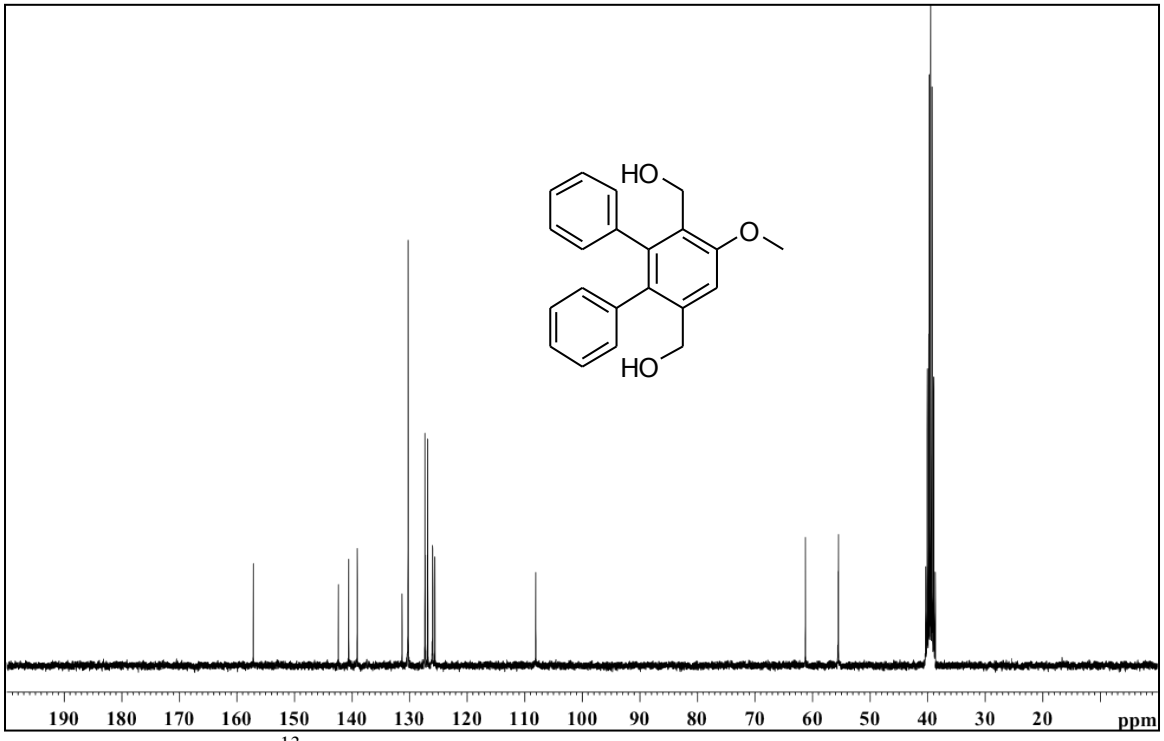


Figure 67: 300 MHz ^{13}C NMR Spectrum (DMSO) of **112a**.

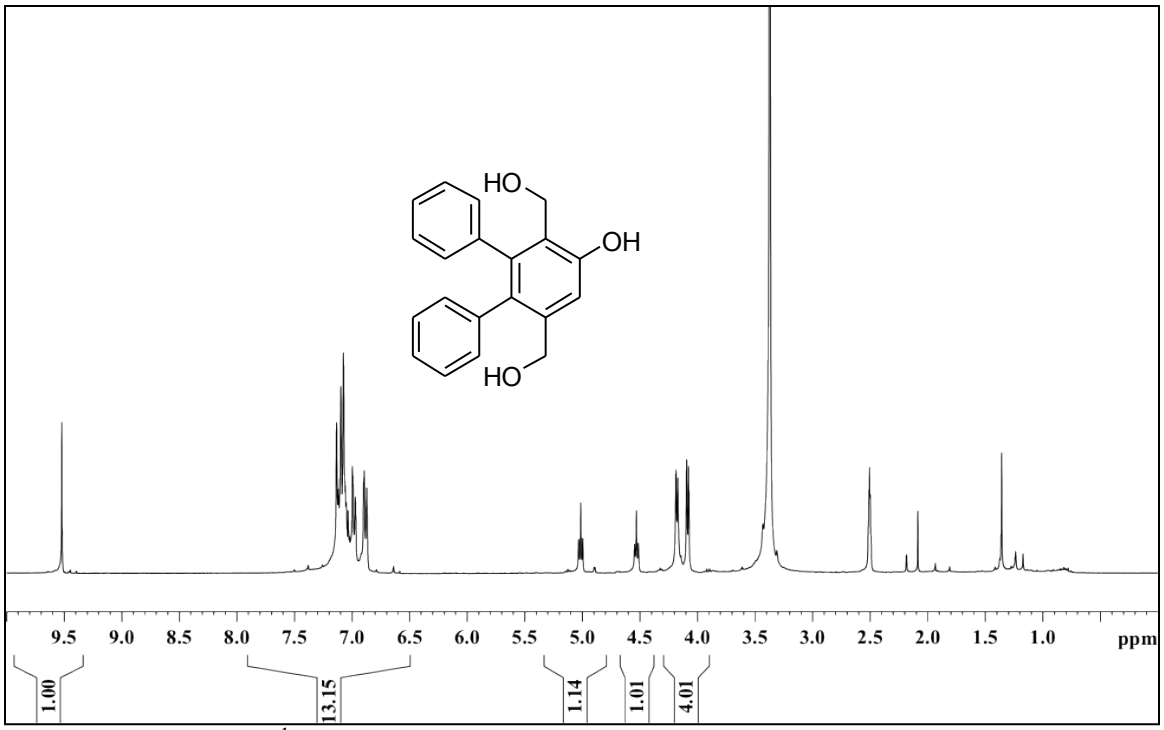


Figure 68: 300 MHz ^{1}H NMR Spectrum (DMSO) of **112b** from **111b**.

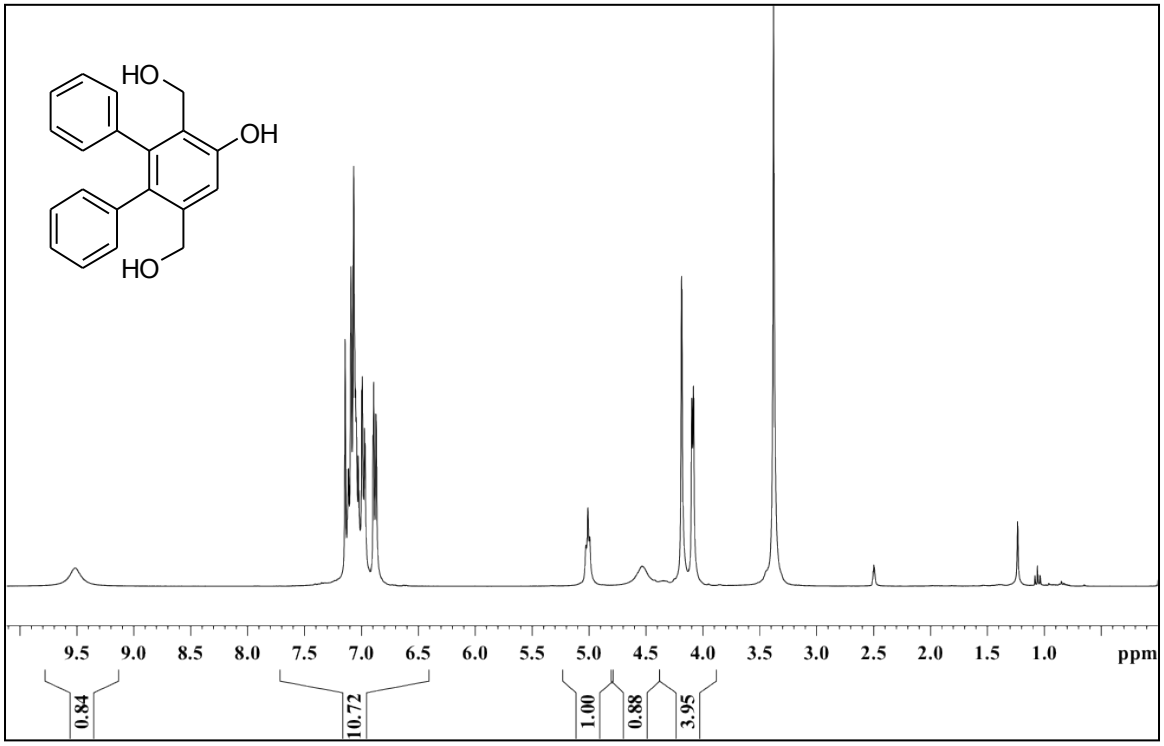


Figure 69: 300 MHz ^{1}H NMR Spectrum (DMSO) of **112b** from **111d**.

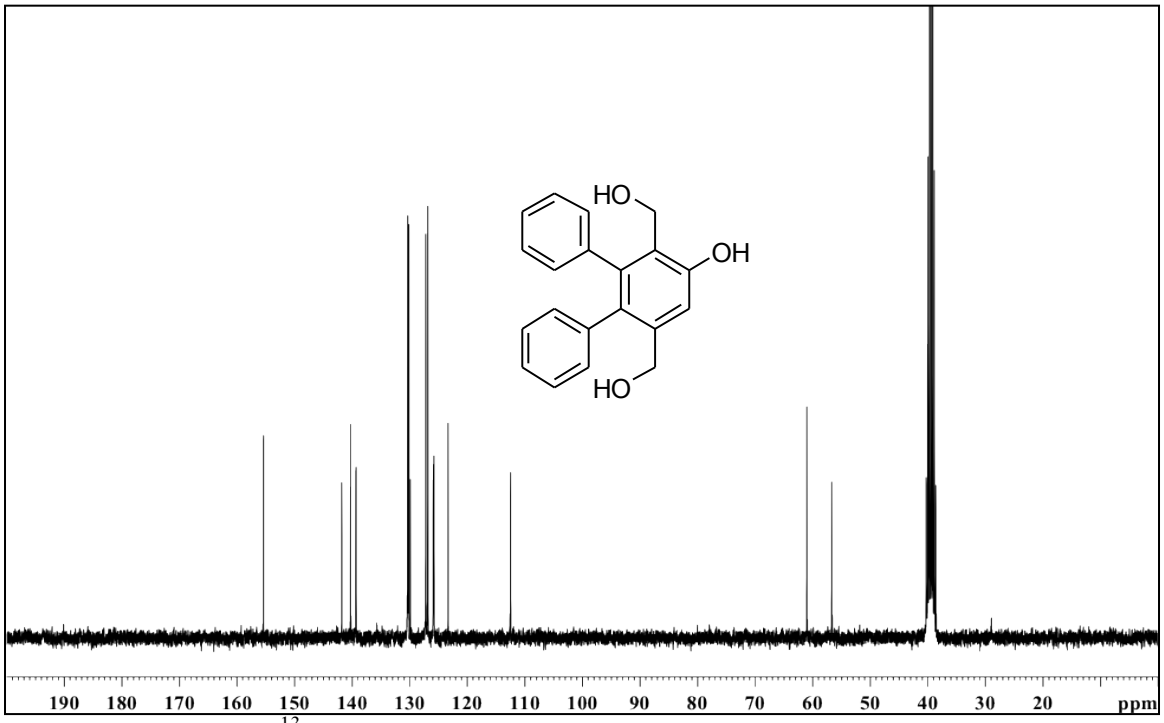


Figure 70: 300 MHz ^{13}C NMR Spectrum (DMSO) of **112b**.

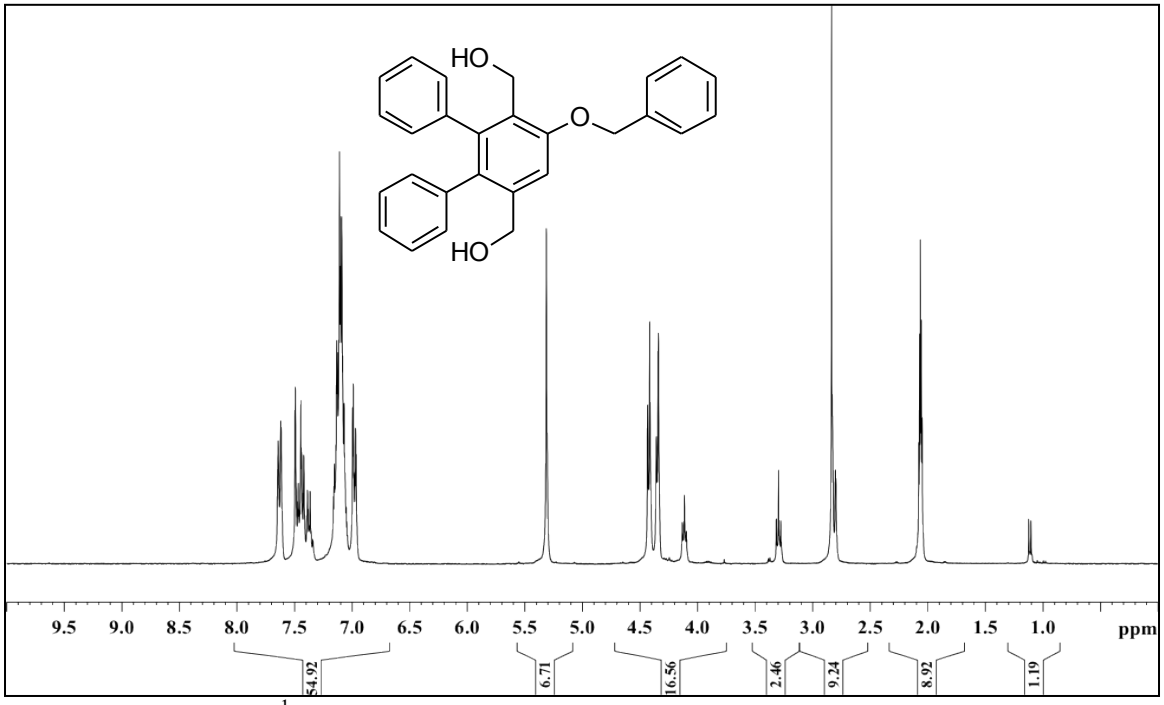


Figure 71: 300 MHz ^{1}H NMR Spectrum (DMSO) of **112c**.

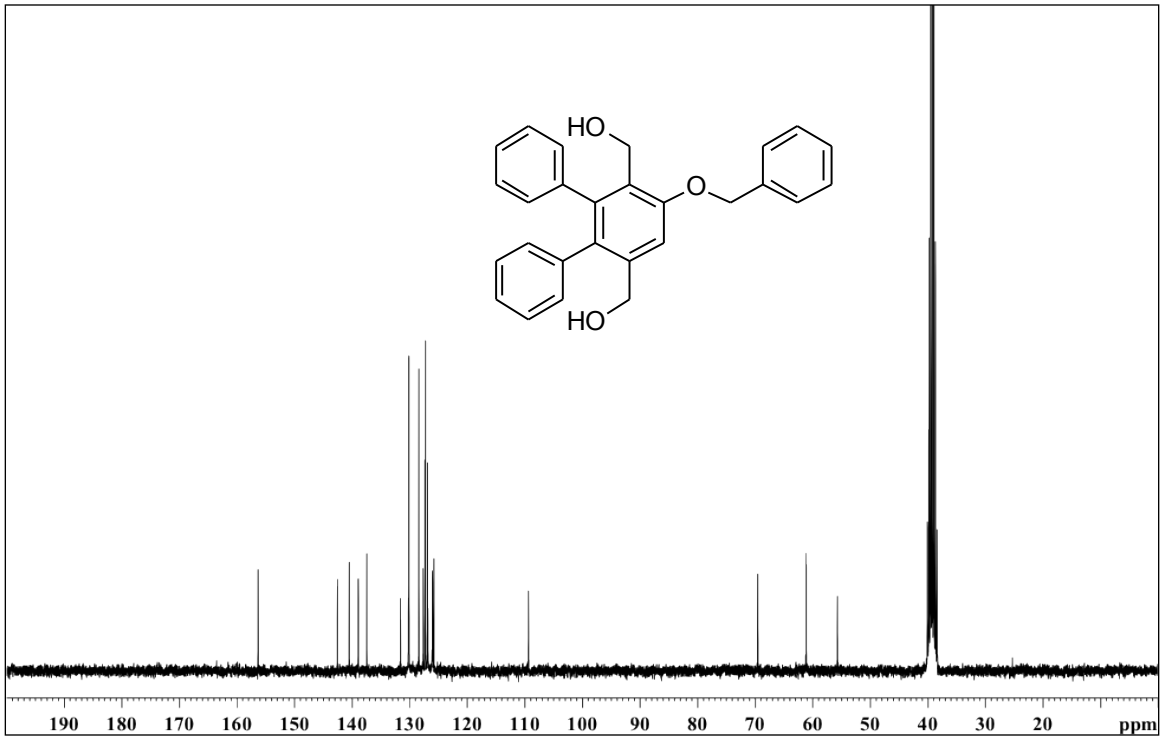


Figure 72: 300 MHz ^{13}C NMR Spectrum (DMSO) of **112c**.

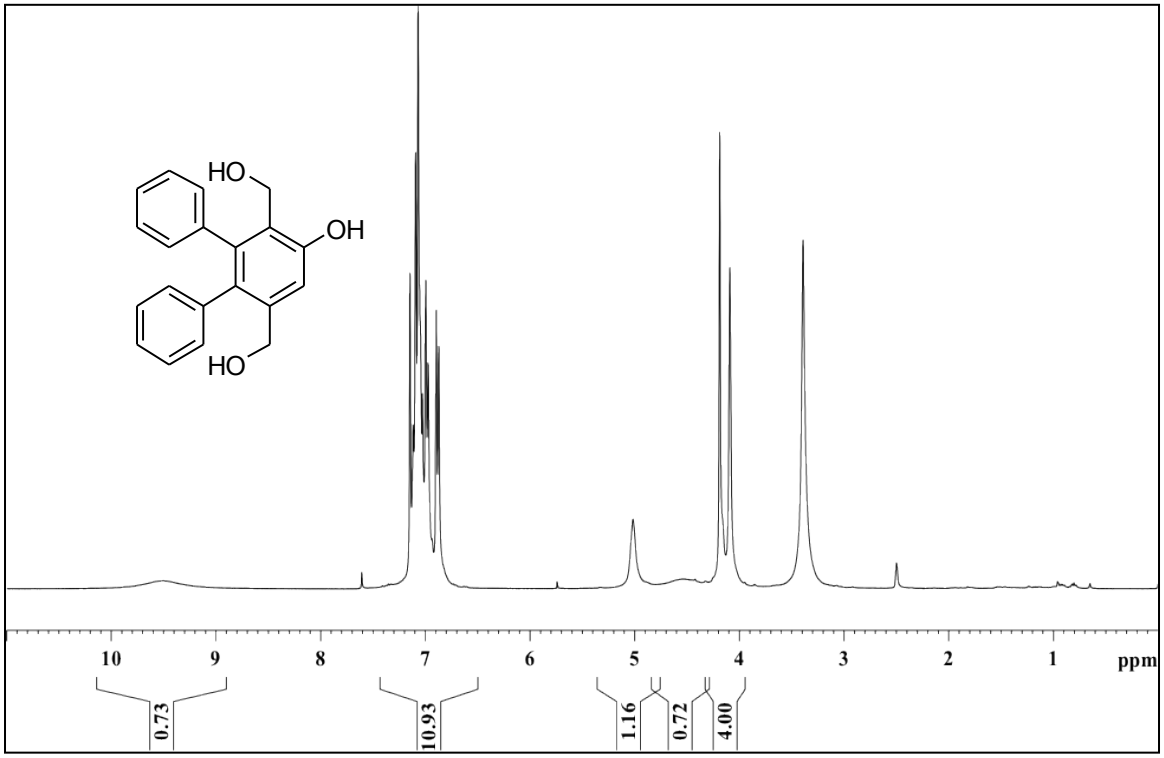


Figure 73: 300 MHz ^{1}H NMR Spectrum (DMSO) of **112b** from **94**.

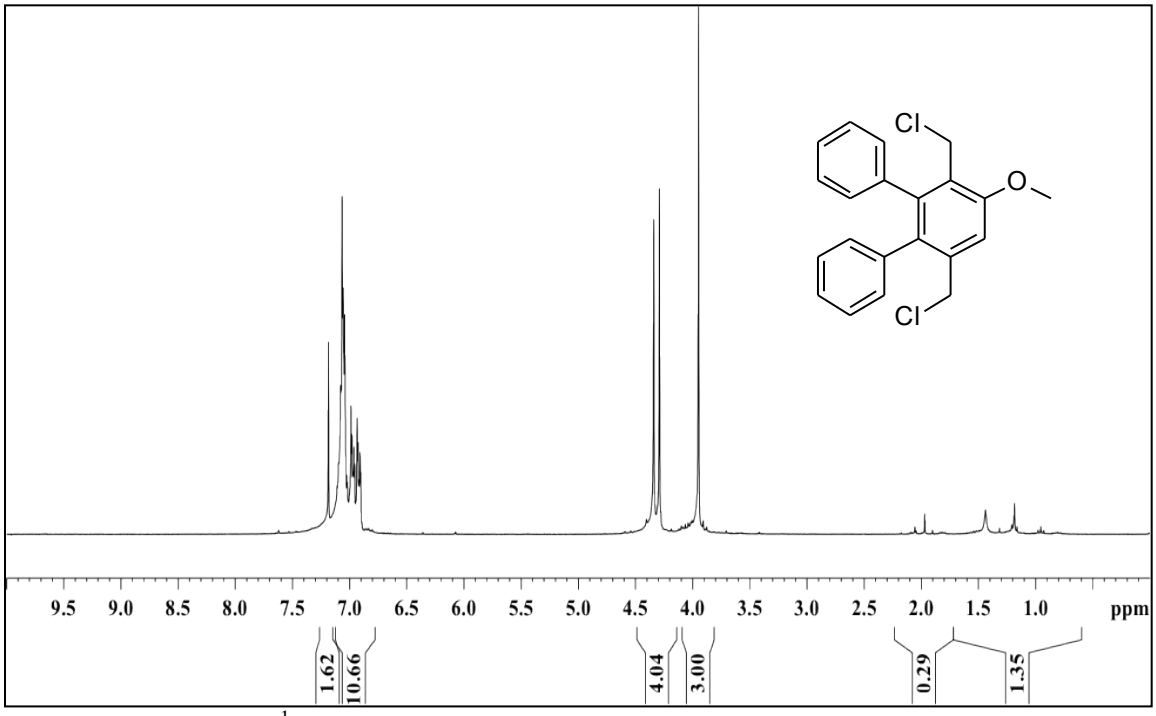


Figure 74: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **113a**.

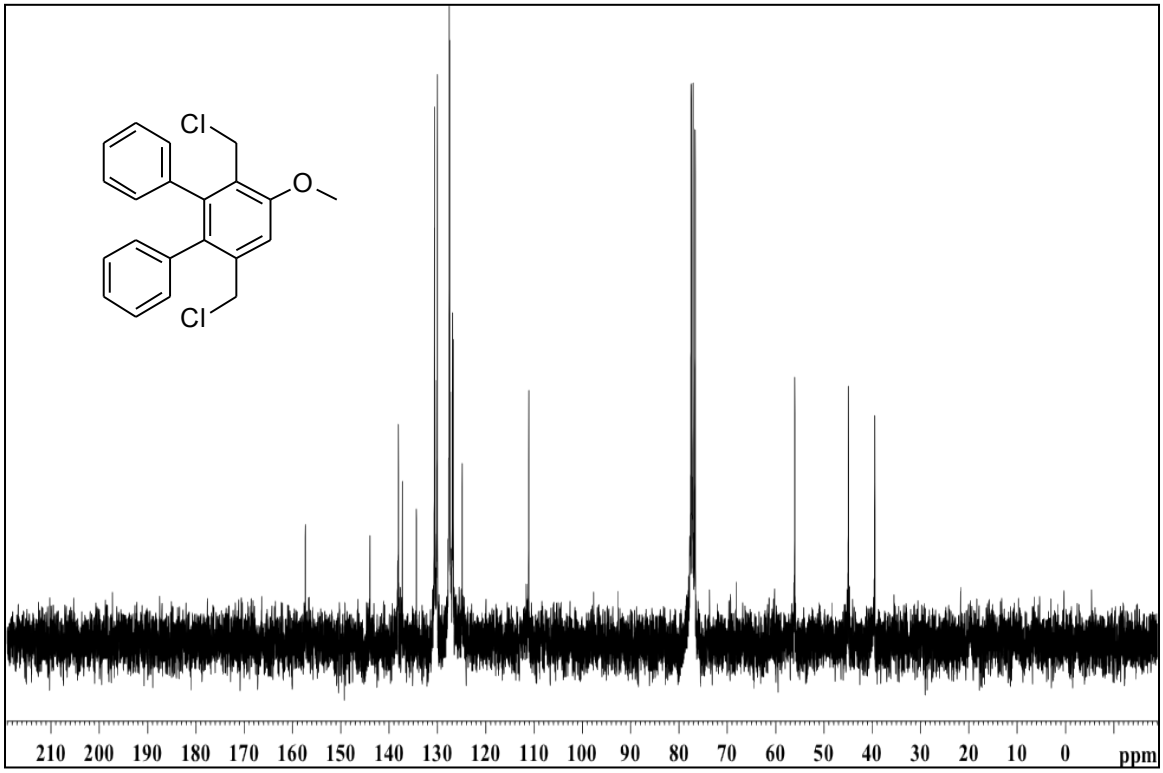


Figure 75: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **113a**.

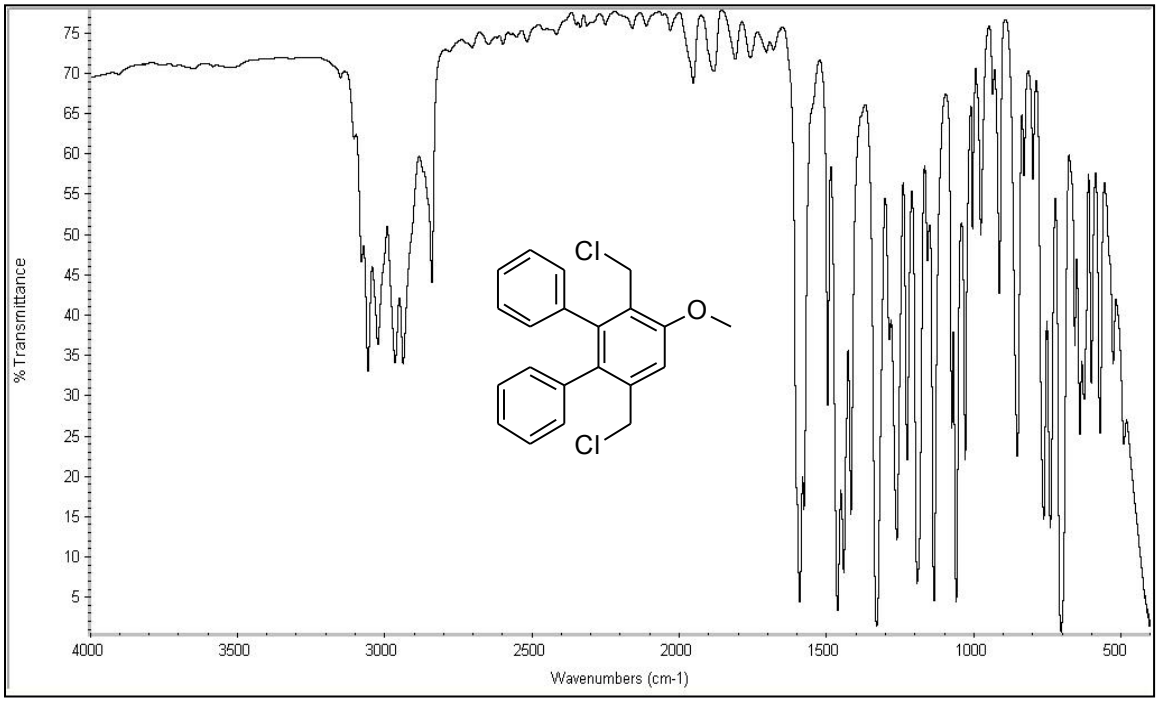


Figure 76: IR Spectrum (NaCl) of **113a**.

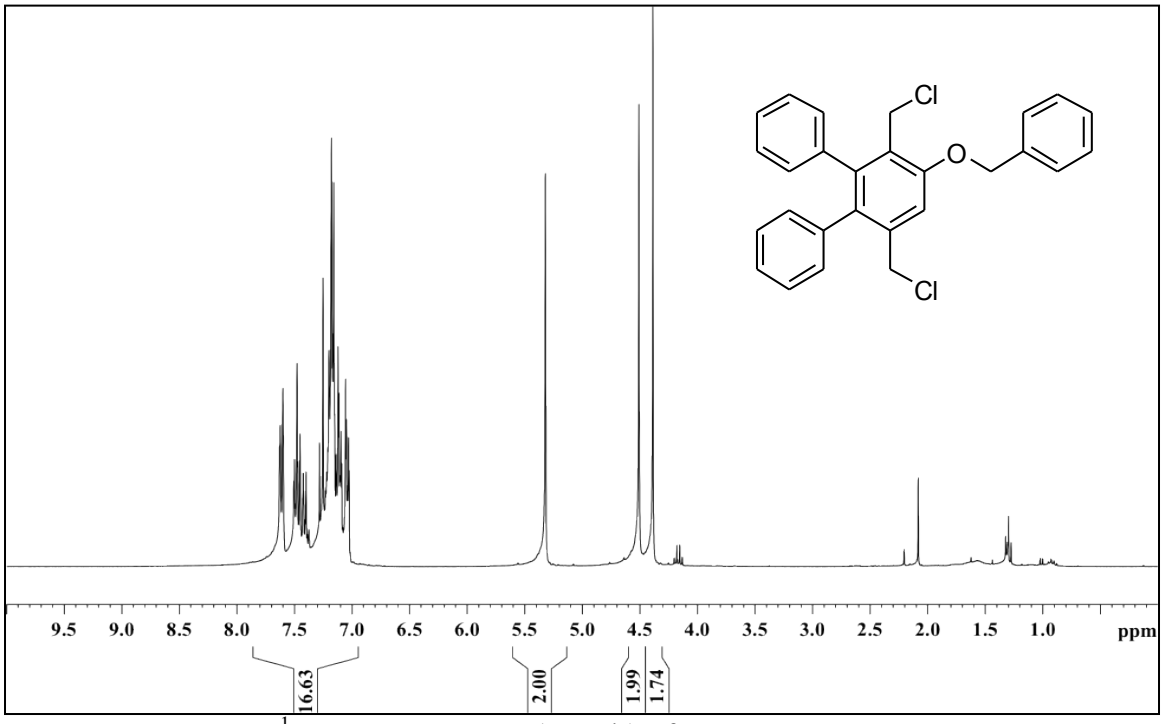


Figure 77: 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **113c**.

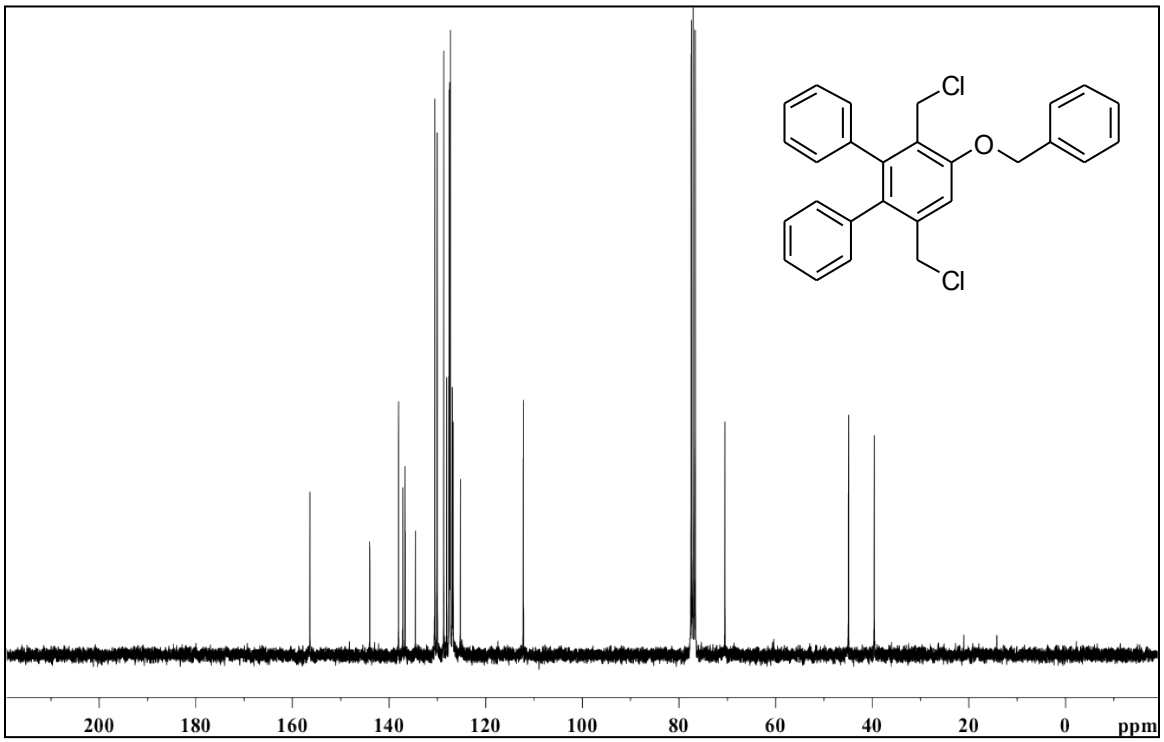


Figure 78: 300 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **113c**.

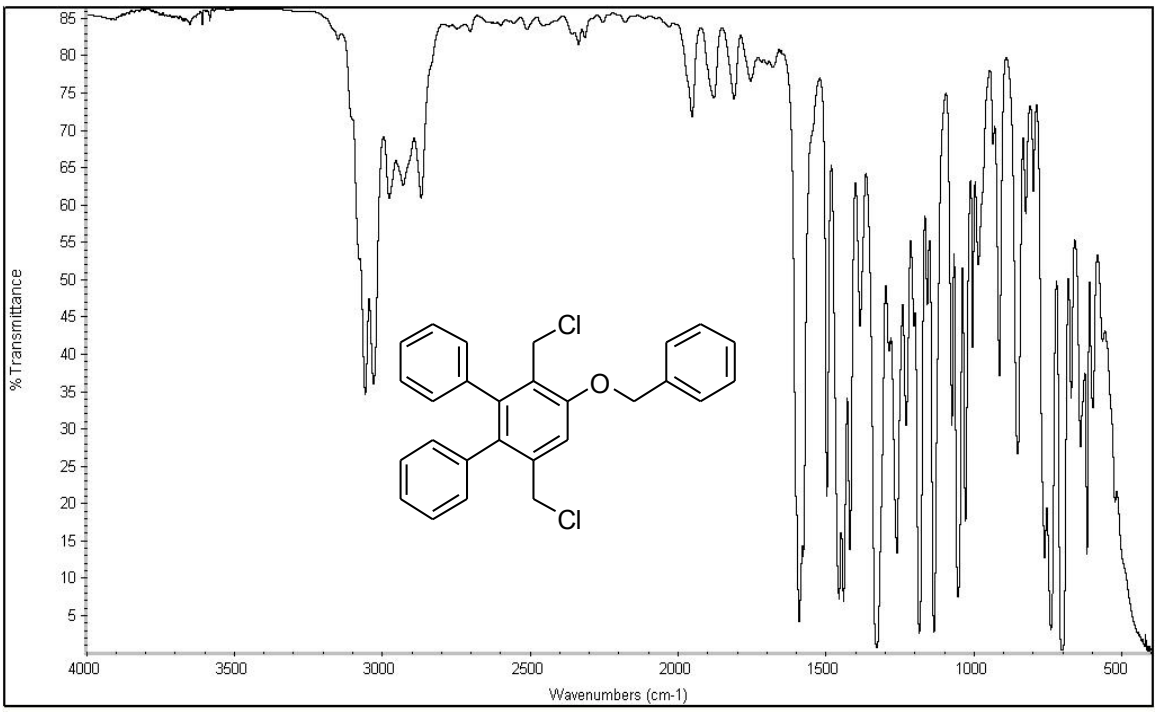


Figure 79: IR Spectrum (NaCl) of **113c**.

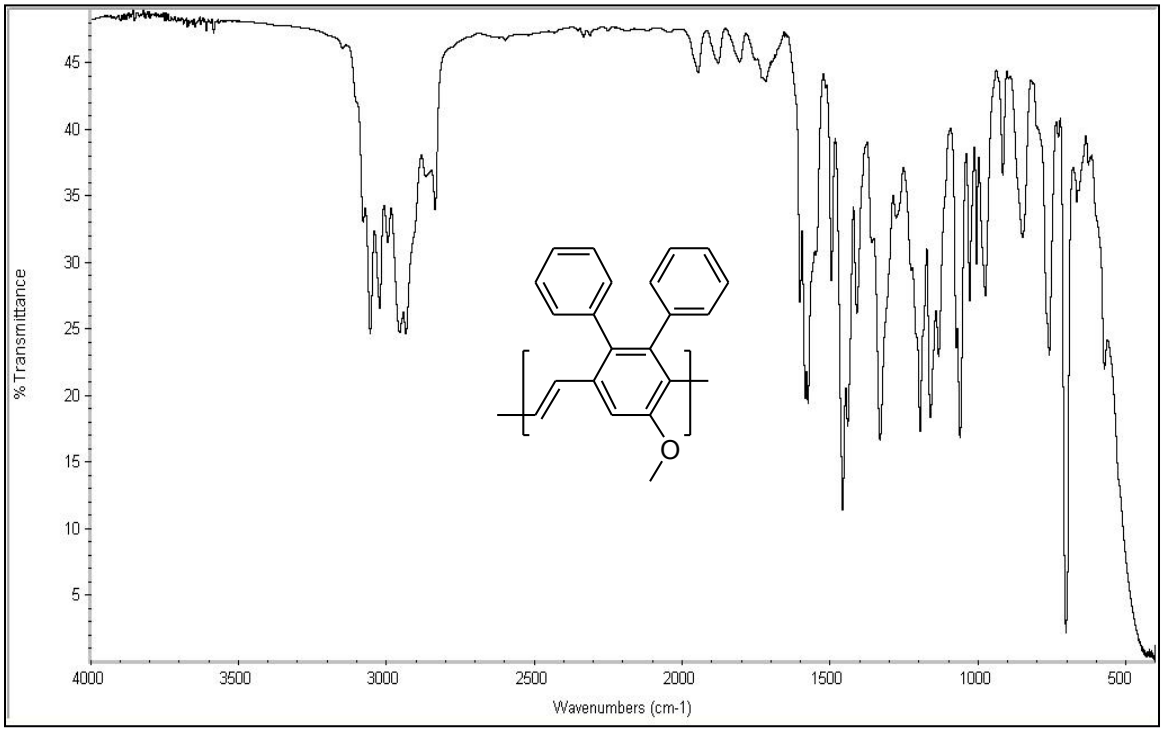


Figure 80: IR Spectrum (NaCl) of **114a**.

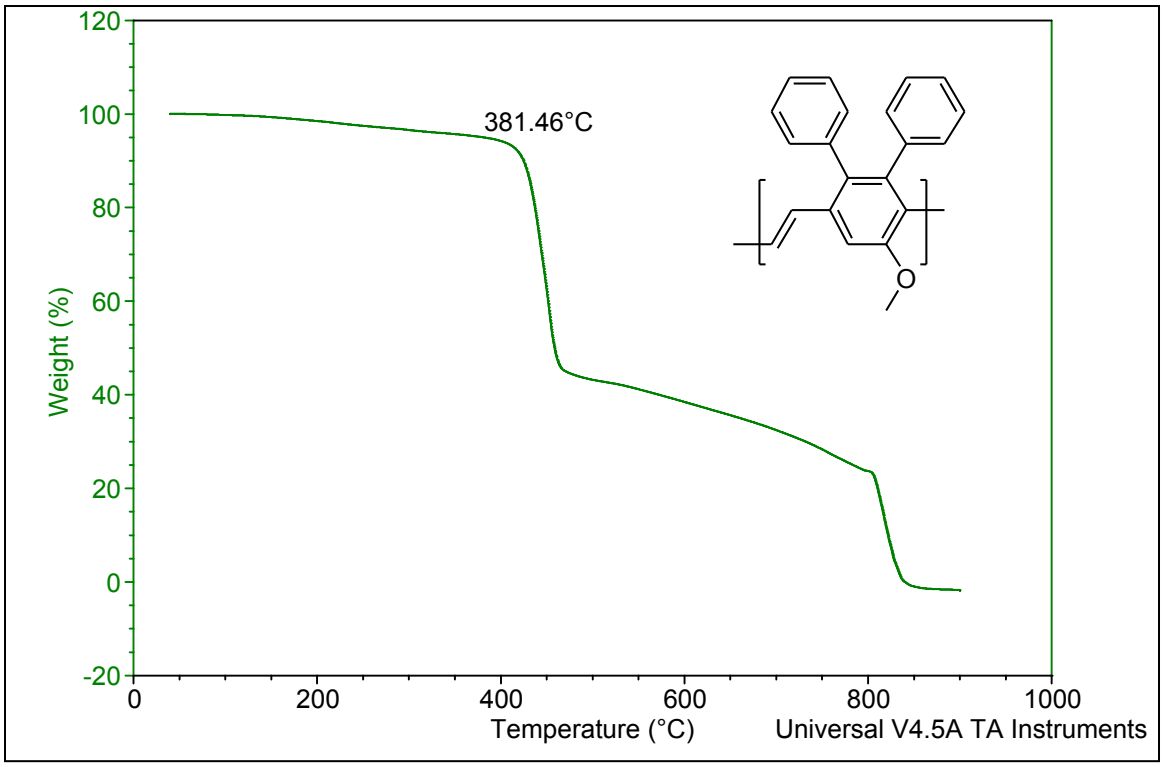


Figure 81:TGA of **114a**.

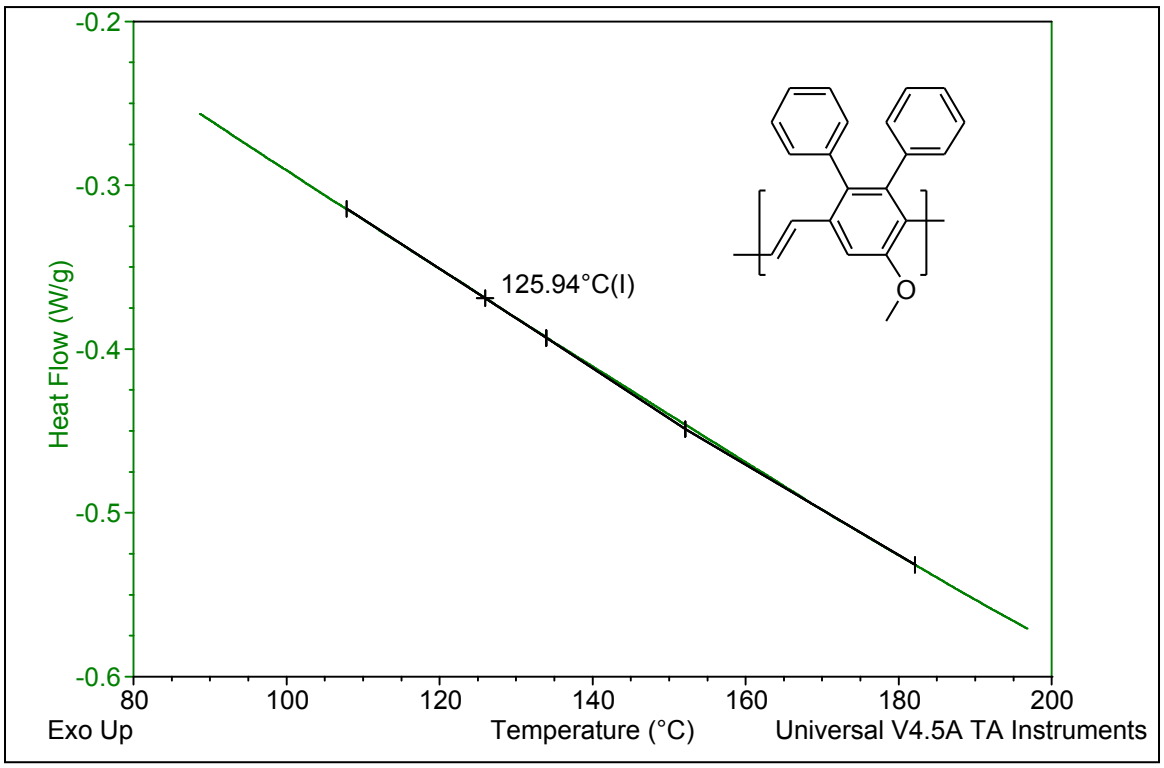


Figure 82:DSC of **114a**.

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VITAE

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